

REPORT

SPR-068
30 November 1971

SOLID POLYMER MEMBRANE PROGRAM

Final Report

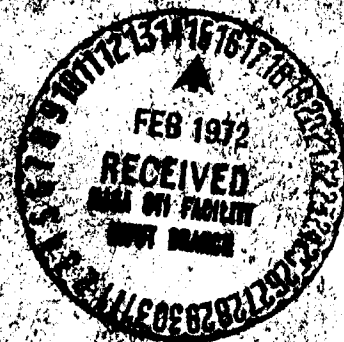
Contract NAS 9-11876

DRL Line Item No. 4

Prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center
Research and Development Branch
Houston, Texas 77058

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DIRECT ENERGY CONVERSION PROGRAMS

AIRCRAFT EQUIPMENT DIVISION
LYNN, MASSACHUSETTS

GENERAL ELECTRIC

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1.0 Foreword

This report summarizes the results of a solid polymer electrolyte fuel cell development program conducted for the National Aeronautics and Space Administration, Manned Spacecraft Center, Propulsion and Power Division, Houston, Texas by the General Electric Company, Direct Energy Conversion Programs, Lynn, Massachusetts, under Contract NAS 9-11876.

The objective of this program was to identify the failure mechanism and to demonstrate the resolution of the failure mechanism experienced in small stack testing under previous Contract NAS 9-11033, Fuel Cell Technology Program. The effort included laboratory analysis and evaluation of a matrix of configurations and operational variables for effects on the degree of hydrogen fluoride released from the cell and on the degree of blistering/delamination occurring in the reactant inlet areas of the cell and to correlate these conditions with cell life capabilities. The laboratory evaluation tests were run at conditions intended to accelerate the degradation of the solid polymer electrolyte in order to obtain relative evaluations as quick as possible. Evaluation of the resolutions for the identified failure mechanism in space shuttle configuration cell assemblies was achieved with the fabrication and life testing of two small stack buildups (4 cell assemblies/8 cells each) designated B/U 101 and B/U 102.

Contract Amendment 1-C effective 30 August 1971 increased the scope of the program to include the fabrication of additional cooling cartridges and anode assemblies as a continuation of the effort under Paragraph 3.3, Component Test and Evaluation, of the Statement of Work. The scope of the laboratory matrix evaluation was also expanded to include the following effort:

- a) Extension of laboratory 3 x 3 inch cell matrix tests to separate the effects of fluoride production from techniques of humidification on platinized vs. non-platinized cells.
- b) Evaluation of effects of removal of cathode catalyst at inlet areas.
- c) Evaluate factors effecting the sluggish behavior of certain cells to activation procedures and load changes.

Effort on this program was expended during the period 3 May 1971 - 30 November 1971.

2.0 Summary

A Fuel Cell Failure Analysis Summary Report, Data Line Item No. 1 of the Data Requirements List of this contract, (SPR-049, dated 1 November 1971), summarized the work performed in analyzing and understanding the parameters that effected the premature failures of the small stacks tested under Contract NAS 9-11033.



The report covers the following areas of investigation:

- a) Post-test or failure analysis on cells from the small stack buildups tested under NAS 9-11033.
- b) Tests performed to simulate the failure conditions outside of operating fuel cell hardware.
- c) Tests carried out in laboratory 3 x 3 inch hardware for the purpose of determining the relationship of various operational or configuration parameters to the observed degradation of the SPE membrane and the subsequent failure that occurred in space shuttle buildups. The report covers the results of testing 58 cells in these matrix evaluations.

The results of this effort indicate clearly that polymer degradation occurs in the dry reactant inlet areas of a cell assembly with the blistering/delamination of the solid polymer electrolyte and the release of hydrogen fluoride to the product water. The ultimate failure being a stress cracking of the polymer in the chemically degraded areas caused by the tendency of the SPE to shrink when dried. The chemically degrading condition is most evidenced by the presence of hydrogen peroxide which apparently attacks the stressed areas of the SPE. However, the exact mechanism for the hydrogen peroxide attack has not been isolated as yet.

Prehumidification of the reactant gas before entry to the active areas was found to be, by orders of magnitude, the most significant factor in reducing the hydrogen fluoride release and the elimination of delaminations. Platinizing of the SPE was found to be the next most significant factor when operating on dry reactants, although a very second order variable to the humidification. Removal of the cathode catalyst in the area opposite the hydrogen inlet showed a reduction in hydrogen fluoride levels and the elimination of SPE delamination when operating on dry reactants.

Combinations of parameters evaluated near the end of this effort indicate that best results are obtained using a platinized SPE in combination with cathode catalyst removal at the hydrogen inlet and operation using prehumidified reactants. All other parameters evaluated appear insignificant, by comparison.

In view of some paradoxical data that has evolved from the matrix testing it is recommended that additional investigations be conducted as part of a follow-on program as follows:

- a) Further 3 x 3 in. hardware tests should be carried out to completely elucidate the various routes of the peroxide mechanism and to explain the detailed cause of delamination.

b) Life tests with 3 x 3 in. hardware should be carried out in other promising configurations to verify the flexibility of various configurations in solving the problem.

c) Polymer Panel activities should be continued to obtain independent and expert inputs relative to the delamination mechanisms.

As a result of the initial data obtained from laboratory matrix evaluations, small stack B/U 101 (4 cell assemblies) was fabricated with the following configuration modifications from the baseline design established for B/U's #4 and #5:

- a. Platinization was eliminated from the SPE.
- b. Recycle wick pads were added on the cathode opposite the hydrogen inlet areas.

In the assembly of the stack ten (10) thermocouples were added in the oxygen side of the cell assemblies to obtain better thermal data on SPE temperature both steady state and transiently during load changes and stop/start procedures. Four (4) water separator tubes, one for each cell assembly, were installed in order to obtain measurements of hydrogen fluoride produced by individual cells.

The life test was operated successfully for 2011 hours at 150°F with both reactants presaturated in external humidifiers. During the 2011 hours of operation and 13 simulated mission cycles the performance of the small stack was essentially invariant. The test was arbitrarily terminated at the 2011 hour point to remove a cell assembly for complete physical/chemical analysis to provide baseline data at this point of operation.

Analysis of the cell assembly removed showed no signs of degradation or delamination. There were indications that the SPE to cooling cartridge frame bond was marginal after the 2011 hours of operation and evidence of some slight bond leakage was found during teardown tests. Therefore a redesign of the oxygen side gasket was made in order to improve backup support to the bonded joints in the stack assembly. The three (3) remaining cell assemblies were reassembled into a small stack test unit and returned for additional life testing.

Small stack B/U #102 was fabricated directly following B/U #101 with the only change to the cell assembly configuration being the removal of the cathode catalyst under the recycle wick pad in the area of the hydrogen inlets. The stack assembly was coupled without the thermocouples of B/U #101 and with a single water separator tube for the four (4) cell assemblies.

The life test of B/U #101 was operated at 150°F with the oxygen presaturated in the external humidifier and with dry hydrogen entering the cell assembly which was to be humidified on entrance by the SPE which was kept wet in that area by the recycle

wick pad on the cathode side. This unit failed after 1762 hours with twelve (12) simulated mission cycles. The performance of this unit was also invariant to the point of failure.

Failure analysis of Cell #1 showed some delamination and degradation in the area of the top hydrogen inlet manifold and failure occurred in one of the delaminated areas. It has been concluded that the top of the cell became dry when the wicking system lost its prime following a facility power failure which shut the test unit down, but left the ΔP applied across the water separator, drying the wicking system. Thus the recycle wick pad, unable to get sufficient water, caused the top hydrogen inlet area to run dry. The hydrogen inlet manifold at the bottom of the cell showed no signs of delamination or degradation, since its recycle wick pad was able to rewet from the water droplets dropping off the cell wetproofing by gravity. The corrective action for this condition is to install a solenoid-operated valve on the product water line such that, as the other services are shut off, this valve will also close equalizing the ΔP across the water separator tube and preventing the drying of the wicking system.

The results of the life testing of B/U's #101 and #102 confirms, in flight weight Space Shuttle configured hardware, that humidification of the reactant gases will eliminate the delamination and degradation of the SPE. Under the proper conditions of reactant humidification the Space Shuttle configuration cell assembly has the capability of at least 2000 hours of life.

3.0 Laboratory Test and Analysis

The matrix evaluation of configuration and operational parameters affecting SPE delamination, degradation and ultimate failure was started in the 3 x 3 inch laboratory hardware during the previous program (Contract NAS 9-11033) and was considerably expanded during the conduct of this program. For continuity and clarity the complete results of the matrix evaluation program through 1 November 1971 is included in this report. The following data is an excerpt from the Fuel Cell Failure Analysis Summary Report SPR-049 dated 1 November 1971.

It was determined that the same degree of SPE delamination could be reproduced in the laboratory 3 x 3 inch cells as was observed in B/U's #4 and #5. Using the accelerated operating conditions of 220°F, 100ASF and concentrated point feed of reactants, the delaminations and high HF release could be reproduced in only sixteen hours when operated with dry reactants. With this baseline set of conditions established, effort proceeded to evaluate the other parameters of operation on a relative basis.

3.1 LABORATORY 3 x 3 INCH CELL PARAMETRIC INVESTIGATIONS TO
DETERMINE PARAMETERS RELATING TO MEMBRANE DEGRADATION
AND DELAMINATION

3.1.1 Experimental

In all tests, gasketed-laboratory 3 x 3 inch hardware was used having a cell active area of 7.2 in.² (1/20 ft²). This hardware is depicted in Figure 1.

A base line, accelerated test condition was selected as:

- a) B/U 4 M and E configuration.
- b) Point impingement of the hydrogen gas, achieved by blocking the H₂ manifold with silicone rubber. This was to assure a worst case inlet drying condition.
- c) 220°F, 48 psig O₂, 43 psig H₂.
- d) Startup by electrical charging.
- e) 100 ASF current densities.
- f) Dry gas feed.

3.1.2 Parameters Selected for Evaluation

The following parameters were selected for the initial evaluation:

Platinized vs. Non-Platinized SPE

This parameter was selected because of the earlier observations that the platinizing process resulted in an unplatinized area at the center of the SPE

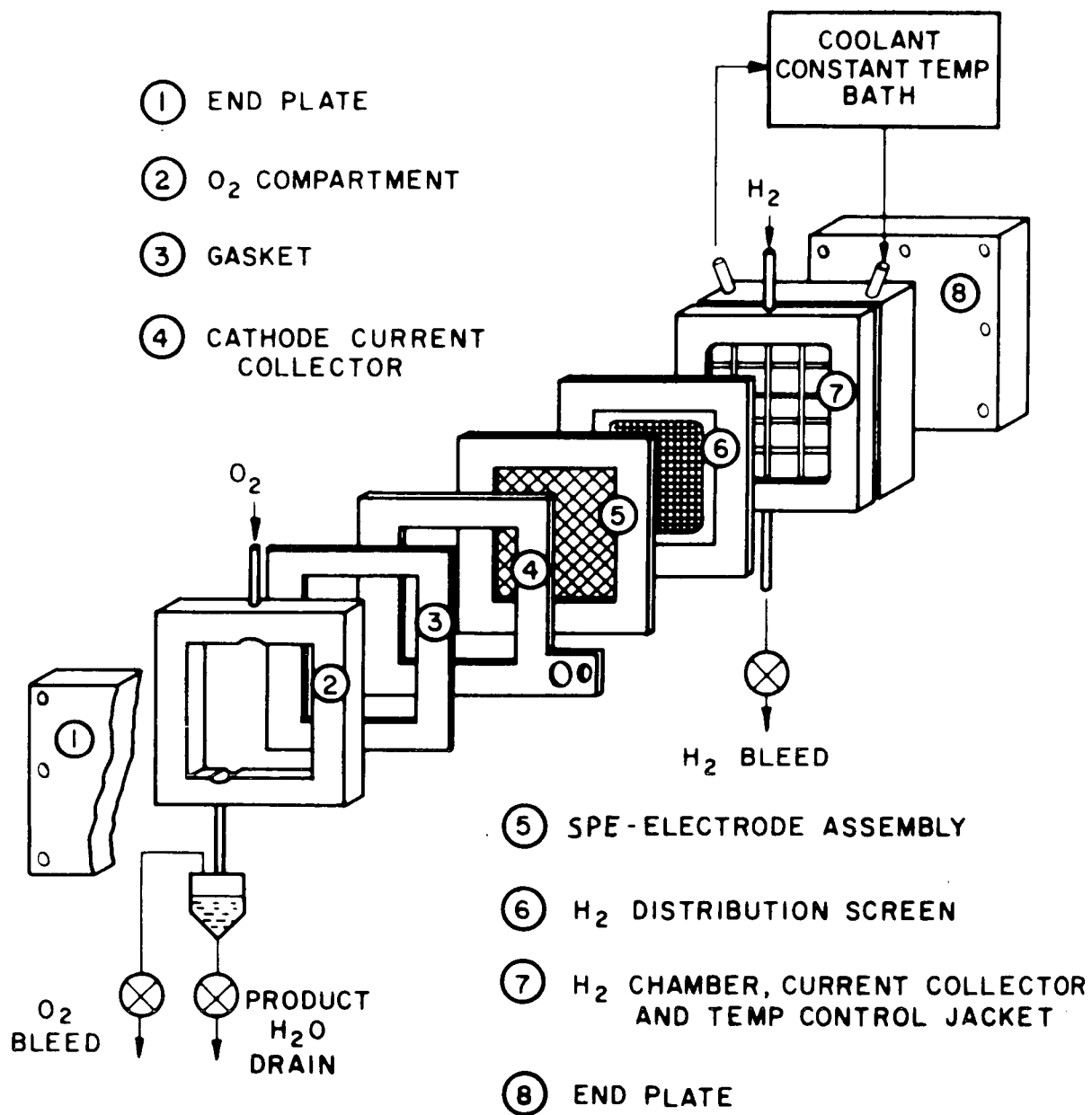


Figure 1. Laboratory 3 x 3 Inch Cell Hardware

Also, the platinizing process requires diffusion of platinum salts into the membrane with subsequent exhaustive reduction by NaBH_4 . Both of these treatments could contribute to the delamination observation.

Extruded vs. Skived SPE

Previous fuel cell programs had utilized a skived membrane. The extruded membrane was introduced to large scale fuel cell hardware for the first time in the Advanced Fuel Cell and Space Shuttle Programs in order to achieve considerable increases in physical properties. While the Advanced Fuel Cell Program AFC 1 and 6 had no problems and have achieved over 9000 and 5000 hours of life, respectively, the incidence of delamination and failure in the Space Shuttle Program resulted in the extruded membrane being suspect.

Wet H_2 vs. Dry H_2

A major difference between the AFC 1 and AFC 6 units referred to above and the Space Shuttle units was a reservoir of water (one inch high) contained in the cathode compartment opposite the hydrogen inlet. This water reservoir tends to saturate the incoming H_2 and prevent membrane dryout and subsequent stressing. Also, the location of all Space Shuttle failures at the gas inlet areas made a membrane drying problem a potential "cause of failure".

Wet O_2 vs. Dry O_2

This was not evaluated in the parametric evaluation. B/U 5, which had operated with prehumidified O_2 , had not delaminated at the O_2 inlet. Thus, the use of wet O_2 had obviously corrected the O_2 inlet delamination observed in B/U's 1 - 4.

Temperature

Temperatures of 150 vs. 220°F would be evaluated to determine the gross effect of temperature.

Pressure

Pressures of 20 to > 60 psia would be evaluated to determine the effects of pressure.

Activation Techniques

Although the deep discharge and electrical charge activation procedures had been shown to be non-related to the observations of HF, delamination and failure, it was felt that they should be factored into this evaluation for further confirmation.

SPE Water Content

The Technology Exploitation program had previously demonstrated that when operated to a stress fatigue failure mode, 38 wt % water SPE's had life-times that were 5 to 7 times longer than 26 wt % water SPE's. Based upon this, B/U's 3, 4 and 5 had operated with high water content (38 wt %) membrane. The premature failures of B/U 4 and 5 resulted in a concern that possibly the high water content membrane was more susceptible to the delamination problem.

Localized H₂ Flow Rate

Investigations into a stress fatigue failure mechanism had established a relationship of life to hydrogen flow rate (locally). It was felt that the relationship of the delamination mechanism to localized H₂ flow rate should also be determined.

Cathode Activity

Since HF production no doubt results from a peroxy attack on the membrane backbone and peroxide is formed as an intermediate at the cathode, it was possible that the state of the cathode may be contributing to the rate of membrane degradation. This relationship appeared quite probable as the Space Shuttle hardware is known to suffer a degree of cathode poisoning from the AF-42 bonding material.

Cathode and Anode Catalyst Loadings

The loadings of both electrodes had been varied throughout the Space Shuttle buildup program as attempts were made to improve both performance and life. Thus the effect of catalyst loading on delamination would be determined to isolate this parameter.

For simplicity in dealing with the results of the relatively large number of parameters, the parameters were assigned numbers of 1 - 11, with letters assigned to the levels of the respective parameters. A key to this index is provided as follows.

Parameter	Level			
	A	B	C	D
1. Platinized vs. non-platinized SPE	Plat.	Non-plat.	-	-
2. Extruded vs. skived SPE	Extr.	Skived	-	-
3. Wet H ₂ vs. dry H ₂	Wet	Dry	-	-
4. Temperature (°F)	150	220	-	-
5. Pressure (psia)	20	63	-	-
6. Activation	Electrical	Deep disc.	-	-
7. SPE water content (wt %)	26	38	50	-
8. Localized H ₂ flow rate (equiv. ASF)	100	500	No pinpoint feed	
9. Cathode activity	Clean/ high sur- face area	Contam.	Low surface area	
10. Cathode catalyst loading (mg/cm ²)	4	8		
11. Anode catalyst loading (mg/cm ²)	4	32		

The base line configuration would be identified as:

Parameter	1	2	3	4	5	6	7	8	9	10	11
Level	A	A	B	B	B	A	B	A	A	B	B

Platinized	Extruded	Dry	220°F	63 psia	Electrical Charge	38 wt % Water	100 ASF	Clean	8 mg/cm ²	32 mg/cm ²
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The shorthand that will be used to represent the base line is:

A A B B B A B A A B B

A deviation from the base line would be:

A B B B B A B A A B B

with the boxed **[B]** indicating that parameter 2 (extruded vs. skived) was changed, the **[B]** indicating a skived membrane.

3.1.3 Results of 3 x 3 Inch Cell Parametric Investigations

A summary of cells included in the parametric investigation is shown in Table I. In an attempt to quantify the results, the total HF released by the cell, the HF release rate, and the degree of delaminations are listed for each cell at the bottom of the table. Arbitrary ratings of G (good), F (fair) and B (bad) have been assigned to each cell as shown in Table I.

Humidified H₂ is Major Parameter

An analysis of the data contained in Table I leads to several significant conclusions. The single most significant can be seen by comparing Cells 122L, 122A, and 126L (A A **[A]** B B A B A A B B) with base line cells 114L and 117L (A A B B B A B A A B B) and 128L (A A B B B A B A A B B). The only difference being parameter 3 (wet vs. dry H₂). The use of techniques to humidify the hydrogen prevented delamination and greatly reduced HF. Furthermore, if all cells that employ techniques for humidifying H₂ are analyzed, no bad result can be found regardless of the level of the other parameters. It is therefore, concluded that wet vs. dry hydrogen is the parameter which overrides all others.

Other conclusions include:

Non-Platinized Membrane is Superior to Platinized Membrane

Direct comparisons can be obtained by

120L ([B] A B B B A B A A B B)	vs.	114L (A A B B B A B A A B B)
118L ([B] A B B B A B A A B B)	vs.	117L (A A B B B A B A A B B)
136L ([B] A [A] B B A B A A B B)		
142L ([B] A [A] B B A B A A B B)	vs.	133L (A A [A] B B A B A A B B)
147L ([B] A [A] B B A B A A B B)		


FOLDOUT FRAME 1





FOLDOUT FRAME 2

Parameter	Base Line		136L	138L	139L	142L	147L	152L
	114L	117L						
1 (Plat. vs. Non)	A	A	B	A	A	B	B	B
2 (Extr. vs. Skived)	A	A	A	A	B	A	A	A
3 H ₂ Water	B	B	A	B	B	A	A	A
4 Temperature	B	B	B	B	B	B	B	B
5 Pressure	B	B	B	B	B	B	B	B
6 Activation	A	A	A	A	A	A	A	A
7 SPE Water	B	B	B	B	B	B	B	B
8 Gas Flow	A	A	A	BC	A	A	A	A
9 Cathode Activity	A	A	A	A	A	A	A	B
10 Cathode Loading	B	B	B	B	B	B	B	B
11 Anode Loading	B	B	B	B	B	B	B	B
<u>Observations</u>								
a) HF - Total μ gm	6220	640	0	434	9201	165	98	306
μ gm/hr	55	40	0	6.9	83.0	2.5	1.5	3.4
b) Total Test Hours	112	16	113	65	111	66	65	91
c) Delamination	Bad	Bad	None	Small	Bad	None	None	None
d) Other Comments			1/4" wick pad and pre-humidified H ₂		cell failed at H ₂ inlet	1/4" wick pad	1/4" wick pad	1/4" wick pad and had gone through bond cycle
e) <u>Significance</u>	B	B	G	F	B	G	G	G
<div>Good</div> <div>Fair</div> <div>Bad</div>								


In all three cases the non-platinized membranes are superior to the platinized.

Extruded Membrane is Comparable to Skived Membrane




The most direct comparison is Cell 139L(A  B B B A B A A B B) vs. base line Cell 114L. Cell 139L produced 88 μ gm HF/hour vs. 55 μ gm HF/hour for Cell 114L. Both delaminated badly. However, Cell 139L failed due to cross-membrane leakage at the H₂ inlet.

Cell 130L(A  B B B A  A A  ) can also be compared to Cell 114L even though parameters 7, 10 and 11 were also changed as these variables were shown to be insignificant factors. Cell 130L produced 39 μ gm/hour HF and a bad delamination which is not significantly different from Cell 114L.

Increased Temperature Increases Rate of Degradation


Cell 125L(A A B  B A B A A B B) operated at 150°F and can be compared directly to the base line Cell 114L. Cell 125L produced an order of magnitude less HF and was only slightly delaminated. This conclusion verifies the assumption made in this investigation that 220°F was an accelerated test condition.

Degradation Increases Slightly as Pressure is Decreased



This comparison was performed at 150°F as the partial pressure of water at 220°F is too high to allow stable operation at 20 psia. Cell 125L(A A B  B A B A A B B) can be compared to Cell 116L(A A B   A B A A B B). Cell 116L had one-fourth the degradation (HF) and no delamination, suggesting that lower pressures reduce the degradation.

Activation Technique has Little Effect on Degradation

Cell 121L, 123L and 124L were fabricated and operated identically with the exception of the activation technique.

121L(A A B B B A B A  B B) standard electrical charge

123L(A A B B B  B A  B B) electrically charge twice

124L(A A B B B  B A  B B) deep discharge activation

All three cells produced large amounts of HF and delaminated badly. Cell 121L produced three times the HF of the other cells. It seemed paradoxical to assume that if an electrical charge was responsible for this, two electrical charges (Cell 123L) would reduce the HF. It was therefore concluded that the higher rate observed on Cell 121L



must be within the range expected for this configuration and that the activation technique had little effect on degradation.

Membrane Water Content Has No Significant Effect on Degradation

Cells 127L and 131L were fabricated and operated identically with the exception of the membrane water content.

127L (A A B B B A B A A A A)

131L (A A B B B A A A A A A)

Both Cell 127L and 131L produced large quantities of fluoride and were found to be badly delaminated. The 39 vs. 55 μ gm fluoride/hour rates on Cells 127L and 131L, respectively, are within the expected base line range.

Reactant Flow Rate Has a Significant Effect on Degradation

Cells 134L and 138L were fabricated and operated to the base line configuration except that both were loaded to 500 ASF and Cell 138L had a slot H₂ feed (2.7 inches long) vs. the base line point feed (\approx .125 inch long).

134L (A A B B B A B B A B B)

138L (A A B B B A B C A B B)

Cell 134L which operated at 5 times the base line reactant flow rate showed no significant change in the HF release rate. Cell 138L with the slot H₂ feed showed what appeared to be a marked reduction in both HF release rate and degree of delamination.

Cathode Activity Has Little Effect on Degradation

Cells 121L, 123L, 124L and 129L were fabricated to the base line configuration with the exception that the cathode catalyst surface area was low (Cells 121L, 123L and 124L) or contaminated (Cell 129L). Each cell was operated to base line conditions, with the exception of the activation procedures utilized on Cells 123L and 124L. The activation procedures were previously ruled out as being insignificant.

121L (A A B B B A B A C B B)



123L (A A B B B A2X B A C B B)




124L (A A B B B B B A C B B)

129L (A A B B B A B A B B B)

Cells 123L, 124L and 129L all appeared similar to the base line results with high HF release and large area delaminations. Cell 121L had the large area delamination but even greater HF release than the base line. This is probably nothing more than the further extension of the expected base line HF release range.

In addition, Cells 136L and 152L can be compared as both were of the same configuration except that Cell 152L had contaminated cathode catalyst, and Cell 136L had prehumidified hydrogen reactant.



136L ( A  B B A B A A B B)

152L ( A  B B A B A  B B)

Both cells released little or undetectable amounts of HF and neither showed any signs of membrane delamination. This showed that contaminated cathode catalyst had little negative effect on a previously demonstrated improved configuration.





Catalyst Loading (Anode or Cathode) Has No Significant Effect on Degradation


Cell 127L can be directly compared to the base line cells as it was fabricated and tested to the base line configuration with the exception of catalyst loading reductions.

127L (A A B B B A B A A  )





This cell had the same degree of HF release and delamination as the base line cells.

Cells 130L and 131L which also had reduced catalyst loading and other configuration changes previously shown to be of low significance, showed high HF and large area delamination.

130L (A  B B B A  A A  )

131L (A A B B B A  A A  )

In addition, Cell 132L with a previously demonstrated improvement and reduced catalyst loading showed only a slight amount of membrane delamination.

132L (  B B B A B A A  )

3.2

LABORATORY 3 x 3 INCH CELL LIFE TESTS TO RELATE
PARAMETRIC MEMBRANE DEGRADATION/DELAMINATION
EFFECTS TO FUEL CELL LIFE

The 3 x 3 inch laboratory cell parametric test program identified the effects of many configuration and operational parameters on membrane degradation/delamination. It also demonstrated the close relationship, for the parameters tested, between the rate of HF release and the observations of degree of delamination:

- 1) Cells having HF release rates of greater than 15 $\mu\text{gm/hr}$ were always delaminated, usually quite badly.
- 2) Cells having HF release rates of less than 5 $\mu\text{gm/hr}$ usually had no delamination or at worst a very small area of delamination (pin head size blister).
- 3) Cells having HF release rates of between 5 and 15 $\mu\text{gm/hr}$ ranged from no delaminations to small delaminated areas, but were never classified as badly delaminated.

The parametric testing didnot, however, demonstrate any relationship between HF release rate/delamination and fuel cell cross-membrane leakage failure. The HF released from the Space Shuttle buildups, the post-failure reactant inlet delamination area observations along with the identification of all the failures being reactant inlet oriented strongly suggested this relationship. A series of 3 x 3 inch laboratory cell life tests was therefore planned in an attempt to define this relationship.

3.2.1

Experimental

The gasketed 3 x 3 inch laboratory hardware was utilized in all the life tests. The base line accelerated test conditions selected were identical to the parametric test base line, with the exception of the reactant flow rates. At or about the 250 hour point of each test, the reactant flow rates were increased to the equivalent of 500 ASF from the normal base line condition of 100 ASF.

The life test base line configuration was:

- a) B/U 4 M and E configuration.
- b) Point impingement of hydrogen.
- c) 220°F, 48 psig O₂, 43 psig H₂.
- d) Startup by electrical charge.



- e) 100 ASF reactant flows for about 250 hours
500 ASF reactant flows from about 250 hours to test end
- f) Dry gas feed

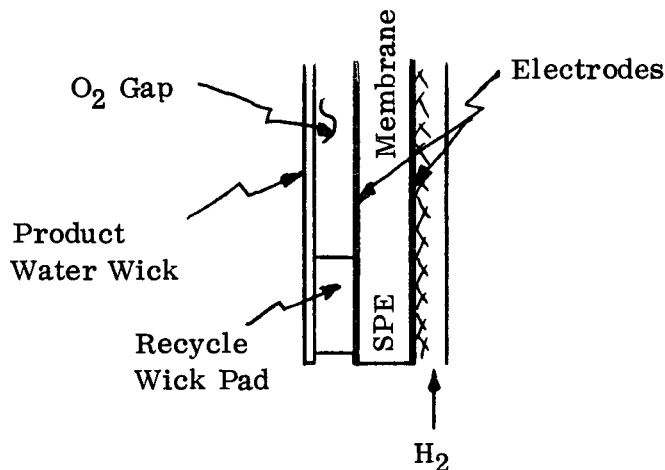
As a result of the Space Shuttle B/U #5 hardware analysis, it was concluded that prehumidification of the oxygen reactant had resulted in the prevention of oxygen inlet area delamination and reduction in HF release, and therefore was not included in the parametric testing as its effect was "known". It was introduced into the 3 x 3 inch life test program to demonstrate significant life differences between the life test base line and the "optimum" life configurations.

3.2.2 Parameters Selected for Life Test Evaluations

The following parameters were selected for the life test evaluations:

Wet H₂ vs. Dry H₂

The parametric test program identified the hydrogen inlet water condition as the major parameter affecting membrane degradation/delamination. The life test base line cells utilized dry reactant, whereas other life test cells utilized prehumidified hydrogen and/or water recycle wick pads. See sketch below.



Platinized vs. Nonplatinized

The parametric test program indicated a significant effect on membrane degradation/delamination, depending upon the existence of platinum within the membrane. The life test base line cell, like all previous Space Shuttle buildups, utilized platinized membrane. The other life test cells utilized nonplatinized membrane.

Wet O₂ vs. Dry O₂

The life test base line cells utilized dry O₂, whereas the other cells utilized the Space Shuttle B/U 5 "proven" parameter of prehumidified oxygen.

Accelerated Conditions



Although high temperature and pressure were identified as increasing membrane degradation and delamination, they were both utilized to accelerate the life testing. In addition, reactant flow rates were increased to 500 ASF equivalent from 100 ASF equivalent at approximately 250 hours into each life test for further acceleration of failure.

All other parameters were held at the parametric test program base line configuration for all life test cells.








3.2.3 Results of 3 x 3 Inch Cell Life Tests

A summary of all cells included in the life test program is shown in Table II.

Base Line Life Test Results

Cell 140L (A A B B B A B A/  A B B A) and Cell 149L (A A B B B A B A/  A B B A) were of the base line configuration. They failed at 261 and 350 hours, respectively, by cross-membrane leakage. Both cells had a large area of delamination at the O₂-H₂ inlet area, with the failure point located within the delamination. The HF release rate was high throughout the testing. Both cells responded in every way as expected.

Configuration No. 1 Life Test Results

Cell 141L ( A _{1,2} B B A B A A B B ₁) and Cell 143L ( A _{1,2} B B A B A/  A B B ₁) represented Configuration No. 1 and differed from the life test base line cells in the following respects:

- a) Both cells utilized nonplatinized membrane.
- b) Both cells had an internal recycle wick pad.
- c) Both cells had prehumidified oxygen and hydrogen reactants.

Life test of Cell 141L was terminated without failure at 65 hours when the HF release rate greatly exceeded that which was expected. Cell 136L of the parametric test

Table II

Accelerated 3 x 3 Inch Cell Life Tests

<u>Parameter</u>	<u>Life Test Base Line</u>		<u>Configuration No. 1</u>		<u>Configuration No. 2</u>	
	<u>140L</u>	<u>149L</u>	<u>141L</u>	<u>143L</u>	<u>144L</u>	<u>148AL</u>
1. (Platinized vs. Nonplatinized)	A	A	B	B	B	B
2. Extruded vs. Skived	A	A	A	A	A	A
3. H ₂ Water	B	B	A _{1,2}	A _{1,2}	A ₂	A ₂
4. Temperature	B	B	B	B	B	B
5. Pressure	B	B	B	B	B	B
6. Activation	A	A	A	A	A	A
7. SPE Water	B	B	B	B	B	B
8. Gas Flow	A/ B	A/ B	A	A/ B	A/ B	A
9. Cathode Activity	A	A	A	A	A	A
10. Cathode Loading	B	B	B	B	B	B
11. Anode Loading	B	B	B	B	B	B
12. O ₂ Water	A	A	B ₁	B ₁	B ₁	B ₁
Observations						
a) HF-Total μ gm	9,855	7,897	1,804	25,370	9,368	15,232
μ gm/hr	38	22.5	28	23.8	15.6	59.5
b) Total Test Hours	261	350	65	1059	598	256
c) Delamination	Bad	Bad	None	Very Small	Small	Very Small
d) Failure Location	Yes in Delam.	Yes in Delam.	No	No	Yes in Delam.	No
e) Significance	B	B	B	B	B	B

Note: Boxed letter indicates deviation from the original parametric base line.

Good = <5 μ gm HF/hr/no delamination

Fair = 5-15 μ gm HF/hr slight or no delamination

Bad = >15 μ gm HF/hr and/or delamination

1. Prehumidified reactant
2. H₂ humidification via wick pad

program, which was identical to Cell 141L except for lack of prehumidified oxygen, produced no measureable HF through 113 hours of testing. A visual examination of the membrane from Cell 141L showed no signs of delamination. This was the first 3 x 3 inch test cell not to show a close relationship between HF release and the degree of membrane delamination.

Cell 143L was subsequently life tested and, like Cell 141L, produced a larger quantity of HF than anticipated. This cell was allowed to continue until it exceeded 1000 hours, at which time it was shutdown for examination. Although a large amount of HF was released from the membrane through the 1000 hours of testing, only a very small delamination was identified in the membrane.

Configuration No. 2 Life Test Results

Cell 144L (\boxed{B} A \boxed{A}_2 B B A B A / \boxed{B} A B B \boxed{B}_1) and 148AL (\boxed{B} A \boxed{A}_2 B B A B A A B B \boxed{B}_1) represented Configuration No. 2 which was the second modification of the life test base line intended to demonstrate improved life characteristics. This configuration differed from the life test base line in the following respects:

- a) Both cells utilized nonplatinized membrane.
- b) Both cells had an internal recycle wick pad.
- c) Both cells had prehumidified oxygen reactant, but hydrogen was not humidified.

Like the Configuration No. 1 cells, both Cell 144L and 148AL released more HF than expected. Cell 148AL was removed from test at 256 hours just before going to the 500 ASF flow rates, for visual examination. A very small reactant inlet area delamination was observed, but it was small compared to the parametric test program in the range of HF release to the degree of delamination relationship.

Cell 144L continued life testing to failure at 598 hours. An examination of the membrane showed a small delamination with the failure hole located within the delamination.

In summary, the life tests showed the following:

- a) Membrane delamination and final fuel cell failure are closely related.
- b) HF release is not necessarily related to delamination or final cell failure.

- c) Configuration No. 1 appeared superior in regard to life considerations. (This configuration was selected for Space Shuttle B/U 101 - reported separately.)
- d) Configuration No. 2 appeared superior to the base line but not as good as Configuration No. 1. (This configuration was selected for Space Shuttle B/U 102 - reported separately.) It is very likely that the wick pad was overpowered by the high hydrogen flow rates at the accelerated condition of 500 ASF, 220°F. As the wick pad was originally intended to maintain a wet membrane at the hydrogen inlet at a hydrogen flow equivalent to 100 ASF, the 500 ASF condition was a severe test of the configuration.

3.3 LABORATORY 3 x 3 INCH CELL TESTS FOR FURTHER INSIGHT INTO THE MEMBRANE DEGRADATION MECHANISM

The 3 x 3 inch cell life and parametric test results, along with the J. P. L. * observed "strain line" within the SPE membrane, led to a series of 3 x 3 inch cell tests for the purpose of obtaining insight into the membrane degradation mechanism.

3.3.1 Experimental

The gasketed 3 x 3 inch laboratory hardware was again utilized in the membrane degradation mechanism investigation tests. The original parametric base line accelerated test configuration and conditions were selected except as noted in Table III.

3.3.2 Areas of Investigation

Group No. 1

The 3 x 3 inch life tests showed that HF release from the membrane was not always related to the resultant visually observed degree of delamination. Although a high rate of HF release might occur, this did not always mean delamination. Whereas if delamination was observed, high HF release had been observed prior to the teardown for visual examination. It was thought that further separation of parameters would identify the variables causing this paradox.

The oxygen prehumidification parameter, as mentioned earlier, was "proven" in Space Shuttle B/U 5 by virtue of reduced HF release and lack of delamination when compared to B/U 4. However, both buildups contained platinized membrane. When selecting parameters for life test evaluation, the two separately "proven" parameters of nonplatinized membrane and prehumidified oxygen were combined with the resultant paradox. Therefore, the parameters selected for further investigation were:

a) Platinization vs. nonplatinization.

b) O₂ prehumidification vs. dry O₂.

* Jet Propulsion Laboratory as part of a NASA "Polymer Panel" formed to investigate possible causes of membrane delamination and failure carried out a microscopic examination of membranes and observed what appeared to be strain lines in the center of the membranes.

Table III
3 x 3 Inch Cell Membrane Degradation/Delamination Mechanism Study

	Group No. 1						Group No. 2			Group No. 3			
Parameter	154L	156L	163L	155L	164L	167L	135L	157L	165L	158L	159L	162L	160L
1. Platinized vs. nonplatinized	<u>B</u>	<u>B</u>	<u>B</u>	A	A	A	A	<u>B</u>	A	<u>B</u>	<u>B</u>	<u>B</u>	<u>B</u>
2. Extruded vs. skived	A	A	A	A	A	A	A	A	A	-	A	-	A
3. H ₂ water	<u>A₂</u>	<u>A₂</u>	<u>A_{1,2}</u>	<u>A₂</u>	<u>A₂</u>	<u>A_{1,2}</u>	B	B	B	B	B	B	B
4. Temperature	B	B	B	B	B	B	B	B	B	B	B	B	B
5. Pressure	B	B	B	B	B	B	B	B	B	B	B	B	B
6. Activation	A	A	A	A	A	A	A	A	A	A	A	A	A
7. SPE Water	B	B	B	B	B	B	B	B	B	B	B	B	B
8. Gas Flow	A	A	A	A	A	A	A	A	A	A	A	A	A
9. Cathode Activity	A	A	A	A	A	A	A	A	A	A	A	A	A
10. Cathode Loading	B	B	B	B	B	B	B	B	B	B	B	B	B
11. Anode Loading	B	B	B	B	B	B	B	B	B	B	B	B	B
12. O ₂ Water	B	<u>A₁</u>	<u>A₁</u>	B	<u>A₁</u>	<u>A₁</u>	B	B	B	B	B	B	B
13. See Note	-	-	-	-	-	-	<u>3</u>	<u>3</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
<u>Observations</u>													
a) HF - Total μ gm	322	3265(1070)	2914(1237)	3262(1352)	1913(731)	605	758	5925	2351	14,142	3268	3115	9054
μ gm/hr	1.95	10.6(6.5)	7.3(5.3)	10.6(7.9)	5.8(3.9)	2.9	6.7	36.0	6.7	118	27.7	22.7	127
b) Total Test Hours	166	313(165)	401(234)	322(172)	331(106)	210	113	167	353	114	118	140	72
c) Delamination	None	None	Very Small <u>8</u>	Bad	Medium <u>8</u>	None	None	None	None	Small Delami- nation was not in center, but near anode	Small	Small to medium	Medium

NOTES:

1. Prehumidified reactant.
2. H₂ humidification via wick pad with cathode removed under wick pad.
3. Cathode catalyst eliminated at reactant inlets.
4. One side hydrolysis of "blown" membrane.
5. One side hydrolysis.
6. One side hydrolysis of "blown" membrane with accelerator.
7. Membrane annealed at 275°C.
8. O₂ humidifier was turned off at 189 hours (1636), 236 hours (1646).

☐ Boxed letters or numbers indicate a variation from original parametric base line.

() Conditions after about one week on test.

- c) H₂ prehumidification and cathode omission with wick pad vs. dry H₂ and cathode omission with wick pad.

Group No. 2

The only identified mechanism for membrane degradation is attack from hydrogen peroxide. It was postulated that the generation of hydrogen peroxide was controlled by diffusion of reactants. It was further postulated that the peroxide was formed on the cathode and diffused into the membrane. A series of tests was performed whereby the cathode catalyst was removed from the membrane at the O₂-H₂ inlet areas (i.e., the area that would normally degrade and delaminate).














Group No. 3

Examination of the membrane material by J. P. L. had identified a "strain" line at a plane in the middle of the saponified membrane, but none in membrane that had not been saponified. It was postulated that the saponification process, which is normally carried on by immersion in an alkaline solution, creates a strain at the center of the membrane due to the slow diffusion of the solution into the membrane and the large volume increase of the membrane as the solution is absorbed. A series of tests was performed on membranes which had been treated to prevent the central strain pattern by saponifying the membrane from one side only and by annealing the membrane.

3.3.3 Results of 3 x 3 Inch Cell Degradation Mechanism Study

Group No. 1

The 3 x 3 inch cells tested in Group No. 1 were:

154L ( A  B B A B A A B B B)
 155L (A A  B B A B A A B B B)
 156L ( A  B B A B A A B B )
 164L (A A  B B A B A A B B )
 163L ( A  B B A B A A B B )
 167L (A A  B B A B A A B B )

Non-prehumidified Cells

Cell 154L differed from Cell 155L in that 154L was nonplatinized while 155L was platinized. Both cells differed from the original parametric base line configuration by virtue of a 1/4 inch wick pad installed on the oxygen side opposite the

hydrogen inlet with the cathode omitted under the pad. Cell 154L was tested for about a week (166 hours) during which time the HF release was low as expected. A tear-down of Cell 154L revealed no membrane delamination.

Cell 155L when tested showed an increased fluoride release rate over Cell 154L. Figure 2 shows the HF release rate of all Group No. 1 cells through the first week of testing. Additional HF release rates beyond the one week are not shown since reactant inlet conditions were modified on several cells at that time. At the 172 test hour point, the O₂ humidifier was turned on and Cell 155L was operated in this mode until failure occurred at the 322 total hour point. A teardown of the cell revealed a large delamination of the membrane, with the failure hole located within the delaminated area. The delamination/failure was outboard of the wick pad area.

O₂ Prehumidified Cells

Cell 156L differed from 164L only in that 156L was nonplatinized while 164L was platinized. Both cells utilized oxygen prehumidification during the first week of testing.

Cell 156L was activated and operated. It had a significantly higher HF release rate than the unhumidified Cell 154L. At the 165 test hour point, the O₂ humidifier was shut off and testing continued to the 313 hour point when the test was terminated. A teardown revealed a black dot at the inlet with no delamination.

Cell 164L released significantly less HF than its nonhumidified counterpart, Cell 155L. At the 186 hour point, the O₂ prehumidifier was shut off and testing continued through a total of 331 hours at which time the test was terminated for visual examination. A medium-sized delamination was located at the O₂-H₂ inlet area.

H₂ and O₂ Prehumidified Cells

Cell 163L differed from 167L only in that 163L was nonplatinized while 167L was platinized. Both cells utilized prehumidified oxygen and hydrogen. The HF release rates from both cells were significantly lower than their O₂ prehumidified only counterparts.

At the 234 hour point, the O₂ prehumidifier was shut off on Cell 163L and operation continued for a total of 401 hours. Only slight delamination was identified on this cell.

Cell 167L stabilized at the lowest HF release rate of any of the Group No. 1 cells and was terminated at 210 hours. No evidence of degradation or delamination was observed on this cell.

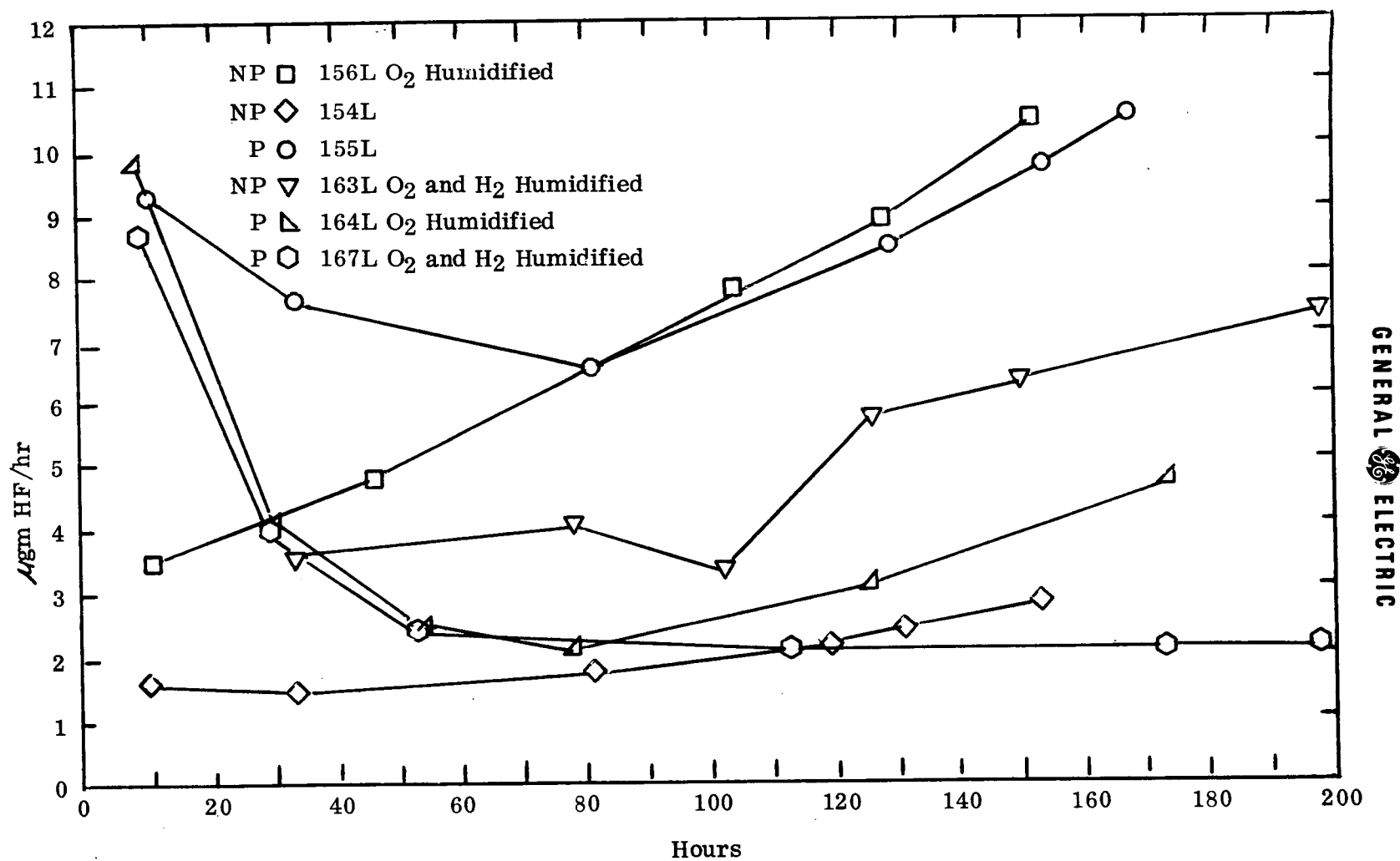


Figure 2. Group No. 1 Test Cells - Fluoride Release

Summary of Group No. 1 Test Results

- a) Initial HF release from platinized cells is significantly higher than on nonplatinized cells.
- b) Hydrogen prehumidification reduces HF release in both platinized and nonplatinized cells.
- c) Oxygen prehumidification significantly reduces the HF release of platinized cells.
- d) Oxygen prehumidification significantly increases the HF release of nonplatinized cells.

Group No. 2

Cells 135L and 165L were of the original parametric base line configuration except that both had the cathode catalyst omitted from the O₂-H₂ inlet area. Operation of the cells showed significant reductions in HF release rates and no delaminations after 113 and 353 test hours for 135L and 165L, respectively.

Cell 157L differed from 135L and 165L only in that it was nonplatinized. It operated for 167 hours with HF release rates significantly higher than earlier counterpart cells without the cathode catalyst removed from the O₂-H₂ inlet area. Although no delamination was identified, it appeared that the anode surface of the membrane at the O₂-H₂ inlet area had undergone chemical degradation as it was flakey in appearance.

In addition, cells 157L and 165L were examined in the O₂-H₂ inlet areas by infrared spectragraph. The results showed significantly more C=O/CF in the unplatinized Cell 157L.

<u>Cell</u>	<u>C-H/HF</u>	<u>C=O/CF</u>
157L	0.08	0.060
165L	0.04	0.004

The results of the Group No. 2 tests have shown that the cathode catalyst must be present to obtain delamination. But, at least in the nonplatinized case, degradation of a modified mechanism is still able to function.

Group No. 3

Cells 158L, 159L and 162L were of the original parametric base line configuration except that they were nonplatinized and that each had undergone saponification from one side. In addition, cells 158L and 162L utilized membrane from a "blowing" process. Although the HF release rate from each cell appeared higher than the nonplatinized base line, the amount of resultant delamination was no more than about the worst that would be expected from the nonplatinized base line. Cell 158 was observed to delaminate near the anode rather than in the center of the membrane. Cells 159L and 162L, however, delaminated in the center of the membrane identically to standard membranes.

Cell 160L was a nonplatinized base line cell which was pre-annealed in the dry membrane form at 275°C (527°F). Both the HF release rate and the amount of delamination were greater than would be expected from the nonplatinized base line.

The Group No. 3 cells indicated that if an internal membrane strain results in the eventual membrane delamination, the two-sided saponification step is not the prime strain-inducing process.

3.4

SUMMARY OF RESULTS

The following is a summary of the results of the investigations reported herein.

- 1) Space Shuttle fuel cell buildup failures were found to be related to dry gas inlet. All failures were located in dry membrane areas. These failures were always associated with delamination/degradation (physical and chemical) of the membrane in the dry areas. Where humidified gases were used, delamination and failure did not occur. High HF production in the product water appeared related to the observed delamination/degradation.
- 2) Attempts to reproduce membrane delaminations outside of fuel cell hardware have been completely negative. Attempts include peroxide exposure, thermal stressing, stress cycling under tension, wet-dry cycling, prolonged autoclaving, as well as a variety of exposures to combinations of the above treatments. It was concluded that the conditions within a fuel cell were unique in their ability to cause degradation.
- 3) Procedural techniques of fuel cell activation such as deep discharge and electrolysis were found to be unrelated to the delamination/degradation. Stop/start procedures were also found to be unrelated.
- 4) Oxygen contamination of the hydrogen at levels of 16,000 ppm did not result in delaminations, high fluoride output, or failure.
- 5) An evaluation of the effect of several variables (platinizing, membrane type, hydrogen humidification, oxygen humidification, temperature, pressure, activation technique, SPE water content, H₂ flow rate, cathode activity, and electrode loadings) showed gas humidity to be the major factor. No delamination was observed at moist gas inlets. Temperature was found to be a significant variable and, within the combinations evaluated in this series, platinized membranes were inferior to nonplatinized membranes. High localized flow of dry hydrogen over the membrane inlet area significantly increases degradation. All other variables had little or no effect.
- 6) Accelerated life tests of 3 x 3 inch cells to evaluate the potential improvement attainable with two improved cell configurations verified that operation with humidified gases could greatly enhance life. The improved configuration was successfully operated for over 1000 hours and upon inspection revealed one "pin head size blister".

The cells (two) operated with dry gases failed at 261 and 350 hours, respectively, and were observed to have large delaminated regions at the gas inlets.

- 7) A subsequent series of parametric tests was carried out to correlate observations of fluoride production with degree of delamination. The major variables were gas humidification and membrane platinization technique. Results showed that it was possible to have modest levels of fluoride production without delamination. However, delaminated cells always had a history of high fluoride production. Oxygen humidification was found to increase fluoride production if cells were unplatinized and to decrease fluoride production with platinized cells. Thus, it became apparent that platinizing in itself was not a primary cause. Hydrogen prehumidification was found to reduce fluoride levels in all cases, and within the variables tested, platinized cells generated more HF than nonplatinized cells.
- 8) A series of cells was operated to determine the effect of removing the cathode in the area of the gas inlets. Removal of the cathode prevented delamination in all cases and reduced fluoride output if the membrane were platinized. However, if the membrane were unplatinized, fluoride rates increased and anode degradation was observed. This suggested that the cathode somehow interacts with other variables to cause delamination.
- 9) After J. P. L.'s observation of potential strains at the center plane of saponified membranes, it was suspected that the saponification technique may be a cause of the membrane delamination. Three cells made from membrane prepared by a "one-sided" saponification technique to eliminate or move the strain from a center plane were tested. All three cells delaminated and produced high fluoride levels. One of the cells delaminated near the anode rather than in the center. However, the other two cells delaminated at the center.
- 10) The ability to operate cells with dry gases without degradation/delamination indicates that physical stresses or membrane strains of themselves are not the cause of the problem.

POSTULATED FAILURE MECHANISM AND POTENTIAL CORRECTIVE ACTIONS

The primary failure mechanism of the Space Shuttle fuel cell is caused by the localized chemical/physical degradation of the solid polymer electrolyte. This degradation, which frequently is manifested by membrane delamination, results in reduced membrane strength which in turn allows failure of the polymer under the normal fuel cell operational stresses. Once the polymer has failed, the cell becomes depolarized by the free mixing of reactants, with resultant decay in cell voltage and automatic shutdown.

Each of the Space Shuttle buildup failures and all of the 3 x 3 inch laboratory cell failures have been related to an area (reactant inlet) of degradation/delamination. The major parameter of the degradation/delamination is the drying effect of incoming reactants. It is postulated that peroxide formed as an intermediate of the catalyst reactions or by reaction of H₂ and O₂ on platinum is greatly concentrated by the dry reactants through water evaporation allowing significant increases in polymeric oxidation.

The location(s) of hydrogen peroxide generation, the peroxide "life" conditions at the location(s), the mode(s) of hydrogen peroxide transport and the influence of internal polymer stress are factors not as yet completely understood and are subject to further testing and analysis.

Several configurations have been identified as having significantly reduced polymer degradation and/or delamination and are therefore less prone to failure. The configuration selected for Space Shuttle B/U 101 demonstrated at least an order of magnitude decrease in degree of delamination (no delamination) although it did not substantially reduce HF release. The B/U 101 configuration was:

Prehumidified O₂
Prehumidified H₂
Unplatinized membrane
H₂ inlet recycle wicking

The 3 x 3 laboratory cell tests have demonstrated that prehumidification of both reactants of a platinized membrane not only significantly reduces delamination but also the HF release rate. With dry reactants, one configuration as demonstrated by Cells 135L and 165L appears promising for future improvement. This configuration utilizes platinized membrane with the cathode platinum catalyst omitted in the reactant inlet area. Both polymer delamination and HF release are reduced with this configuration.

4.0 COMPONENT TEST AND EVALUATION

4.1 Fabrication and Test of B/U 101

A complete report of the fabrication, testing and teardown analysis of this unit is contained in SPR-053, Component Test and Evaluation Report - Small Stack B/U 101.

4.1.1 Summary

The small stack life testing and associated failure analyses performed under Contract NAS 9-11033 concluded that premature failure was caused by physical and chemical degradation of the solid polymer electrolyte membrane at the dry gas inlets of the cell assembly. Based on these conclusions, the following corrective actions were incorporated into the design and operation of Buildup No. 101"

- 1) The design of the cathode side of the cell assembly was modified to remove the porous Teflon wetproof film in the area adjacent to the H₂ inlet channels and covering these areas with a Dacron felt wick pad to recycle product water to the SPE, replacing that removed in the humidification of the incoming hydrogen.
- 2) Thermocouples were placed in the cathode compartments to measure temperatures at the H₂ and O₂ inlet areas and other selected cathode and wick locations.
- 3) Individual product water systems were incorporated in each of the cells in order to measure fluoride content in the water produced by each assembly.
- 4) Prehumidified hydrogen and oxygen were used during the endurance test to insure minimum drying and stressing of the SPE membrane at the reactant gas inlets.
- 5) Non-platinized SPE membranes were used in all cells in B/U 101 since the platinum in the membrane was shown in 3 x 3 inch laboratory tests to contribute to degradation and delamination at the gas inlets. The teardown analysis of B/U 3/3A, which had successfully completed 2000 hours of endurance testing, was found to have developed minute bond leakage at the gold bus bar-to-membrane interface. As a corrective action, an improved bus bar-to-membrane bonding technique was incorporated into B/U 101.

After fabricating B/U 101, it was tested successfully for a total load time of 2011 hours with the completion of 13 mission cycles. At the end of the endurance test, the unit was shutdown and stored with oxygen on both sides at 3 psig and at room temperature until teardown.

The teardown analysis of B/U 101 showed all membranes to be in excellent condition. However, the membrane-to-cell frame bond was found to be marginal in strength and one cell exhibited minor leakage through this bond interface.



The reactant gas inlet areas of the cell assembly analyzed were free of delamination and showed no significant signs of polymer degradation.

Conclusions drawn from this test are that the design and operational changes incorporated into B/U 101 were effective in preventing failure conditions at the gas inlets. However, the bond system appears to be marginal along the hydrogen inlet manifold sides of the cell assembly where the oxygen side gasket was relieved.

The components of the water removal subsystem checked out satisfactorily at teardown except that the wicks appeared to be dry and hydrophobic. It is postulated that the wicks were drained and lost prime during the facility shutdown when the product water valve was left open, thus imposing a continuous ΔP across the water separators.

Corrective actions resulting from the teardown analysis include the following:

- 1) Modify facility to provide automatic shut off of the product water valve in the event of shutdown.
- 2) Modify O₂ gaskets to provide greater bond support. Reassemble buildup with remaining three cells to test this modification.

4.1.2 DESIGN

All of the design changes to the base line design of the cell assembly, which were introduced in B/U 4 and 5, were retained in B/U 101. The cathode side of the cell, however, was modified in B/U 101 to incorporate the hydrogen humidification configuration mentioned in section 4.1.1.

4.1.2.1 Membrane/Electrode Configuration

All of the buildups prior to B/U 101 used SPE membranes containing platinum as a peroxide decomposition catalyst designed to extend the life of the cells. During the failure analysis of B/U 4, it became apparent that the presence of the catalyst may have contributed to membrane delamination and degradation at the reactant gas inlet areas. Laboratory tests on 3 x 3 inch cells also indicated an apparent relationship between the rate of fluoride production and the tendency of cells to delaminate. It was therefore decided to eliminate the platinization process from the cells in B/U 101.

As in previous buildups (B/U 3 and later), the membrane used was the extruded stabilized "R" type autoclaved to give a high water content of 36 to 40% by weight.

Catalyst loadings were as follows:

Anode: 30 mg/cm² catalyst blend

Cathode: 7.9 mg/cm² catalyst blend

After the discovery of minute areas of leakage through the gold-membrane bond interface during the teardown analysis of B/U 3/3A, an improved bonding system was devised which could readily be introduced without major hardware changes. The modification to the existing design consisted of curing a layer of AF-42 adhesive to both sides of the anode bus bars and adjacent electrode screen just prior to the fabrication of the membrane/electrode assembly. The subsequent bonding of the membrane/electrode assembly to coolant cartridge hardware remained unchanged.

Laboratory tests conducted on samples of this new bond system indicated superior life when aged in water at 200°F. Apparently, the precured AF-42 coating on the gold, which is applied in a dry environment to the anode assembly, produces a longer life bond than was obtained when cured in the presence of the wet membrane. The AF-42 completely encapsulates the anode screen in the area between the bus bar and the active area of the cell, thus minimizing the possibility of leakage along the screen strands.

The configuration of the cathodes in B/U 101 was modified such that the LNP wetproof film was cut back .32 inch at the top and bottom sides of the cells. This allowed an unrestricted flow of water from the H₂ humidification pads into the membrane in these areas. In B/U 101 the cathode catalyst was retained in this cut back LNP area.

As in previous buildups, the standard hydraulic mold method was used to assemble the electrodes to the SPE membranes.

4.1.2.2 Cell Assembly Configuration

The cell assembly, consisting of the coolant cartridge, two hydrogen system compartments and two membrane/electrode assemblies bonded into a single package, remained unchanged from the design used in B/U 4 and 5. The compartmentalized H₂ cavity with two H₂ inlet channels at top and bottom was used. The catalytic scavengers in each H₂ inlet channel were retained.

4.1.2.3 Oxygen System Configuration

In order to saturate the inlet hydrogen as it passes across the membrane, the following changes were made to the oxygen system opposite to the H₂ inlet areas:

- 1) The O₂ system frame was cut back slightly at top and bottom to provide additional space for the H₂ humidification pads.
- 2) H₂ humidification pads (Dacron felt) were bonded to the O₂ system frame as shown in Figure 3.
- 3) The O₂ distribution screen was cut back at top and bottom to provide room for the H₂ humidification pads.
- 4) The design of the O₂ tube guard was modified at the O₂ purge tube so that it would not cover the H₂ humidification pad in that area.

The changes introduced in B/U's 4 and 5 to increase the saturation of inlet O₂ (i. e., long O₂ inlet tube placed behind the product water wick and the second layer of wicking in the O₂ inlet area) were retained in B/U 101.

4.1.2.4 Stack Assembly Design

Except for the addition of three extra water separators and the installation of thermocouples on cells 3 and 4, the design of the B/U 101 stack assembly was identical to B/U 4/5. The water system and thermocouple locations are described in section 4.1.3.

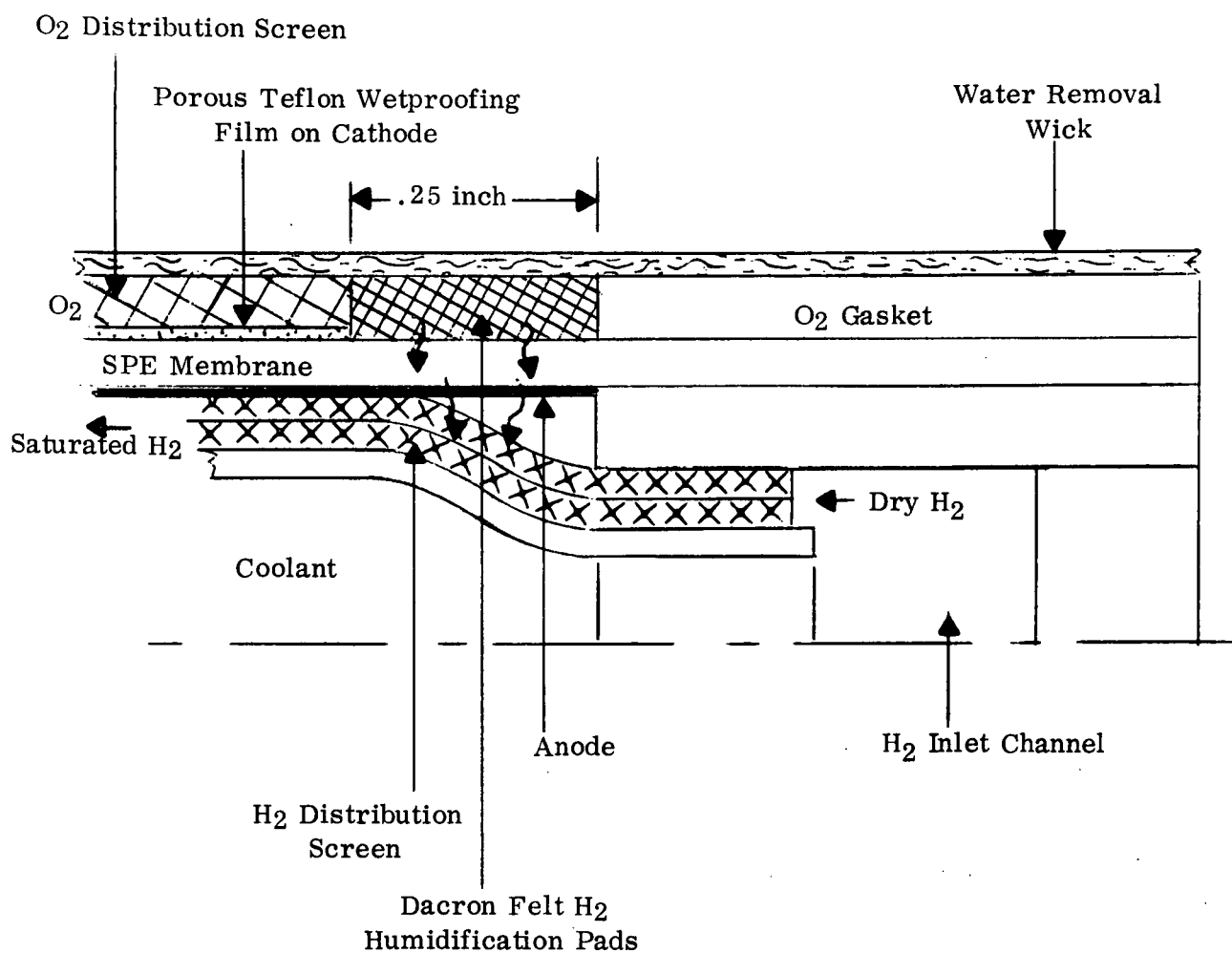


Figure 3. Bonding of H₂ Humidification Pads to O₂ System Frame

4.1.3 FABRICATION

Buildup 101 was fabricated during May 1971. Special thermocouples were installed for measuring temperatures at various points on the cathodes and product water wicking of two of the cell assemblies. Four individual water separators were installed to separately collect water from each of the cell assemblies for analysis. Non-operating leakage and electrical tests were conducted during the various assembly operations.

4.1.3.1 Membrane/Electrode Fabrication

The SPE membranes for B/U 101 were processed in the usual manner except for omitting the platinizing procedure normally performed prior to autoclaving. Also prior to autoclaving, the membrane conditioning process is performed to remove by acid exchange any contamination resulting from handling and inspection up to this point. Autoclaving produced water contents within the 35 to 40 weight percent range.

The fabrication of the cathodes followed the standard procedure except that the LNP porous Teflon film was perforated to facilitate trimming back after cell assembly.

After the fabrication of the anode assemblies by the standard procedures and just prior to the assembly of the electrodes to the membrane, AF-42 prebonds were applied to both sides of the anode bus bars as shown in Figure 4.

The membrane/electrode assemblies were fabricated by the hydraulic mold method except that a 1 mil thick Teflon film was placed between the AF-42 prebond and membrane to prevent adhesion during the high temperature-high pressure cycle.

4.1.3.2 Cell Assembly Fabrication

The membrane/electrode assemblies were bonded to coolant cartridge assemblies to form the cells for B/U 101.

After the bonding cycle, the cathode LNP porous Teflon was peeled back and trimmed along the perforations. Some difficulty was encountered in removing the porous Teflon adhered to the catalyst.

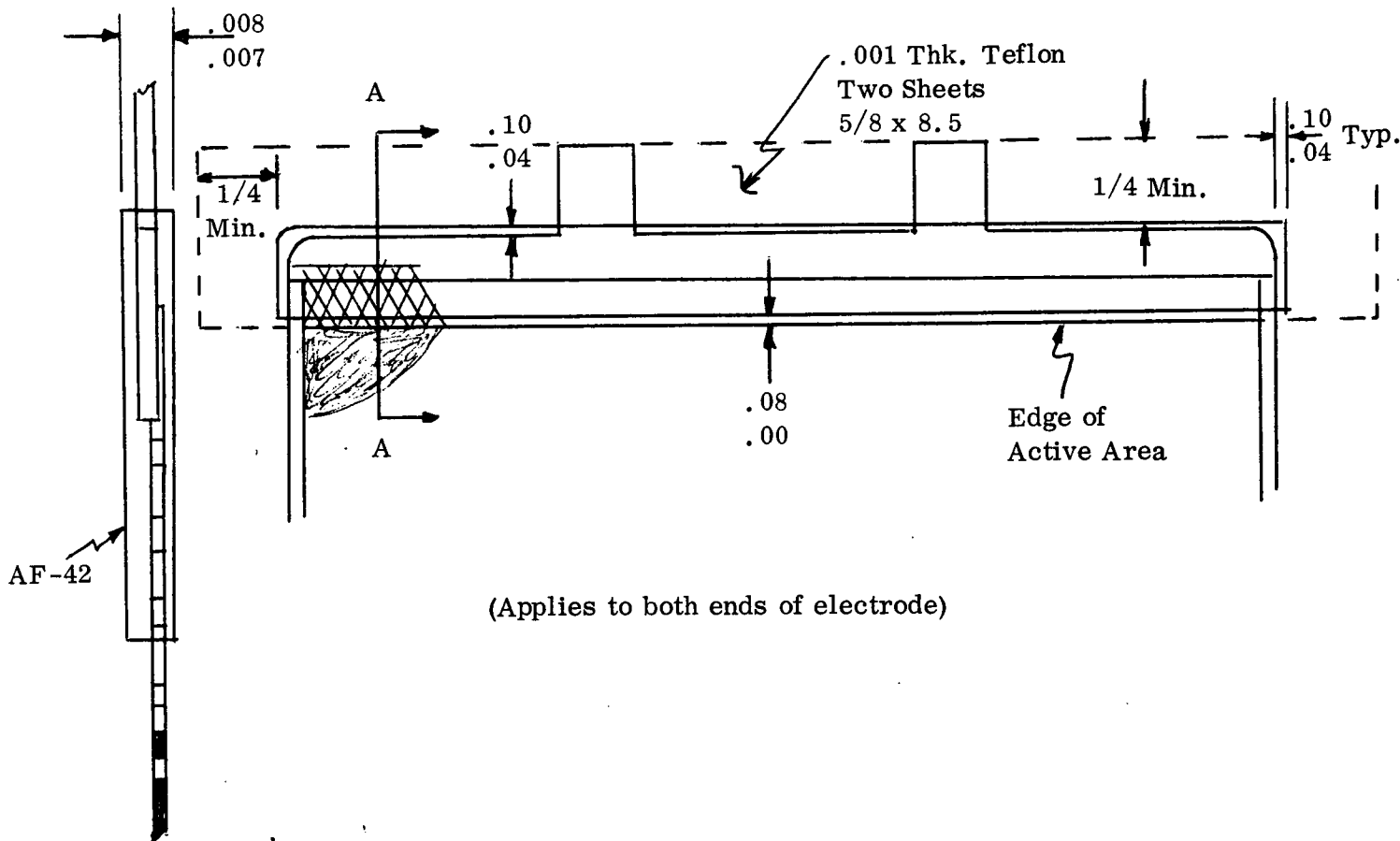


Figure 4. Anode Bus Bar Prebond with AF-42

4.1.3.3 Four-Cell Stack Assembly

During the assembly of the stack, ten platinel thermocouples were installed in various locations on cell positions 3 and 4 to measure temperatures of the cathode surface and opposite wick near the reactant gas inlets and outlets and at the coolant outlet. Figure 7 shows the locations of these thermocouples. A thermocouple was also used to measure the temperature of the wicks. The differential temperature between the cathode and the wick indicates the drying effect that may occur at these locations.

After the assembly of the stack, four individual water separators were installed so that the product water from each cell could be measured and analyzed. The final buildup assembly test results showed a normal O₂ to H₂ side diffusion rate of 31.5 cc/hr at a 27 inch Hg vacuum on the hydrogen side. Cooling system showed zero leakage at 10.4 inches Hg vacuum. The assembly of B/U 101 was completed and shipped to test on 5/27/71.

4.1.4 TESTING

4.1.4.1 Test History

Buildup 101 was installed in Stand No. 8 as shown in Figure 5. Gas humidifiers were used to saturate inlet hydrogen and oxygen. Preliminary leakage tests were performed prior to activation which indicated normal diffusion rates at mission pressure conditions.

Unit activation began on 6/2/71 when a short electrolysis was performed in order to evolve H_2 at the anode. This was followed by a deep discharge and then another electrolysis. The final electrolysis activation was performed to remove excess water from the cathode where it had become trapped during the manufacturing process. The deep discharge procedure consists of electrically pumping hydrogen ions from the anode to the cathode where they displace oxides absorbed during the high-temperature manufacturing processes and contamination accumulated during assembly. Following the second electrolysis cycle, a 40 amp load was applied for the start of Mission 1. Considerable oxygen purging was required during the first hour on load to clear the test case of inerts. After 17 hours on load, the O_2 purge cycle was reduced to 5 seconds every 30 minutes. This cycle was retained through the first 500 hours of the endurance test. The purge cycle was then reduced to 5 seconds every 60 minutes with no apparent effect on performance. The reduced cycle was continued throughout the remainder of the life test.

The cell performance levels were in the same range as experienced on previous buildups. Figure 6 is a chronological plot of current and voltage vs. time for the duration of the 13 mission test. Operating conditions were maintained at 45 psia oxygen pressure and 150°F coolant inlet temperature. Figure 6 shows the approximate power profile for each mission cycle.

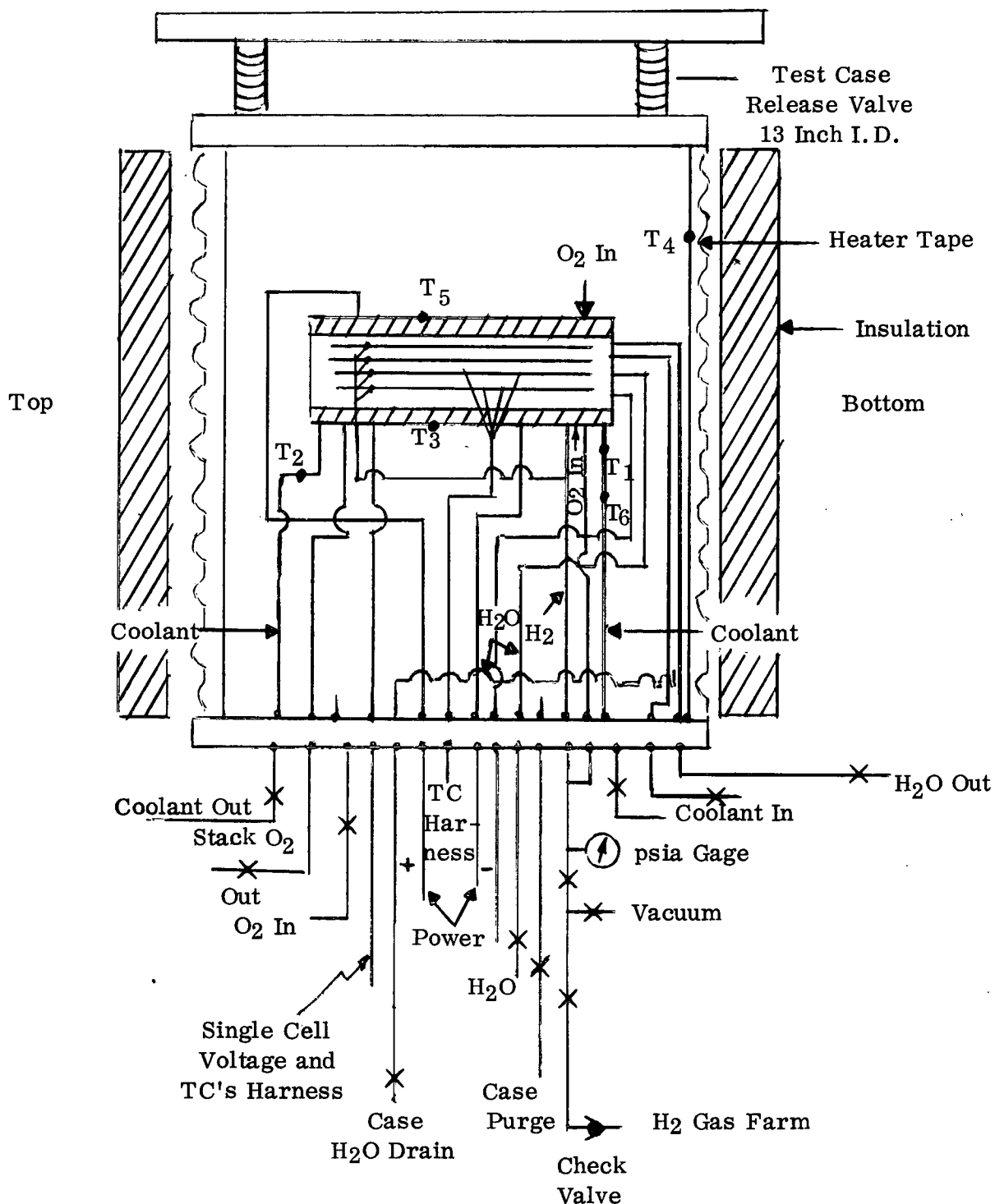


Figure 5. Buildup 101 Test Configuration

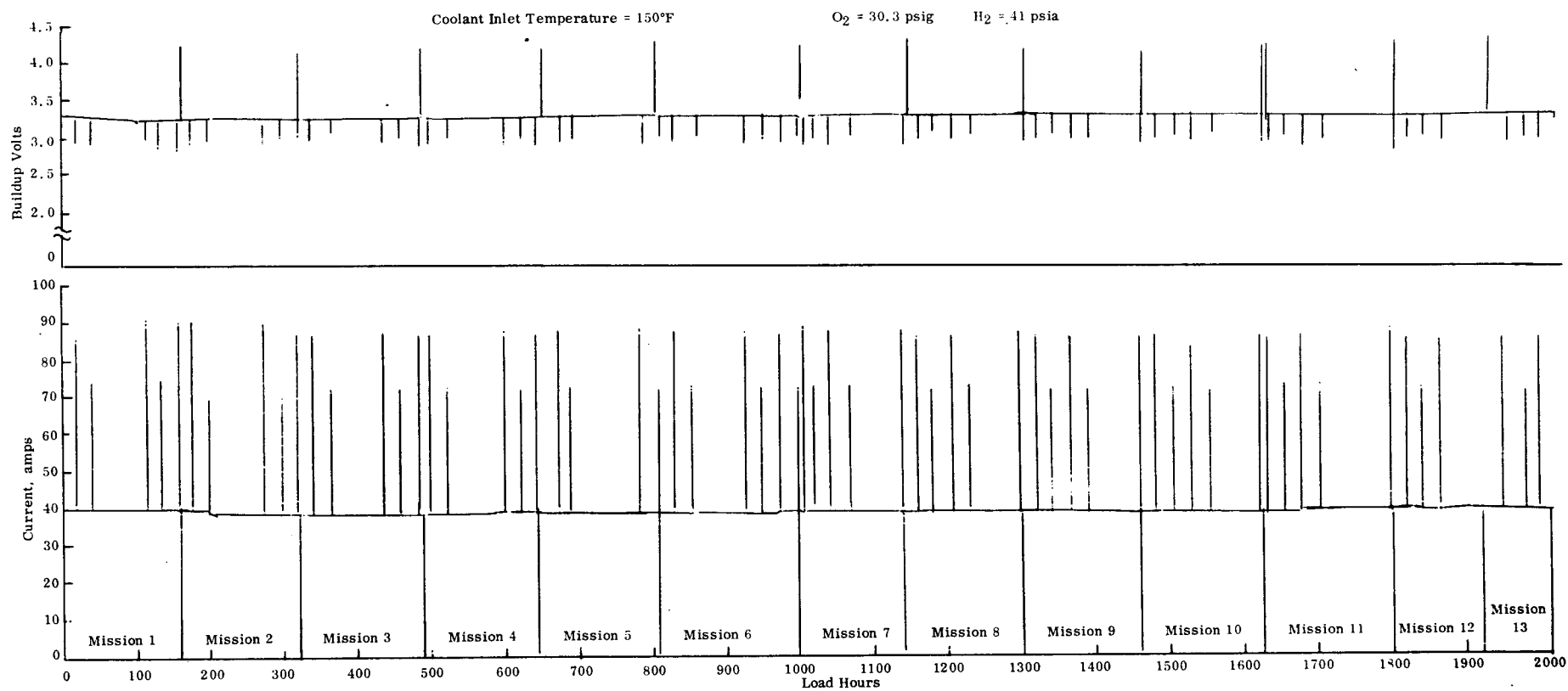


Figure 6. Buildup 101 (4 Cells) Test Performance

During the test, product water samples were taken for bacteriological analysis as well as for the determination of fluoride release rates. Section 4.1.4.3 summarizes these results.

Early in the life test it was noted that the internal platinum thermocouples indicated the actual coolant inlet temperature to be 5 to 7°F higher than measured on the coolant tube wall thermocouples. Thermal insulation was installed to the front panel of the test case and around the coolant lines, resulting in closer correlation between internal and external thermocouples. The coolant inlet temperature was accordingly reduced 6°F. Section 4.1.4.2 summarizes the results of the temperature study. The mission cycle life test continued through six complete missions and 1000 hours, when the unit was shutdown and stored on oxygen at 5 psig over a two-week vacation period. It was restarted for Mission 7 on 8/3/71 with a normal electrolysis start at 10 amps for 10 minutes. The life test continued uneventfully through nine missions. During the tenth mission at the 1634 hour point, a facility coolant pump failure resulted in the automatic load removal from the buildup. From this point, some unpredictable product water delivery rates were observed. Less than theoretical water was removed through the separators and the balance was removed from the test case drain. The performance of the cells, however, was not affected.

At the completion of Mission 11 (1802 hours), a slight increase in the discharge rate of cell 4 during O₂ takeover was observed. Up to this point, cell 1 was the first to discharge. In addition, a hydrogen system leakage test showed a slight increase in the O₂ to H₂ system leakage rate of from 28 to 40 cc/hr. Similar results were observed at the end of Missions 12 and 13. Otherwise, the cell performance under load was not affected.

During Mission 12, a general plant power failure resulted in the automatic shutdown and O₂ takeover of the unit. It was restarted for the continuation of endurance testing. At the end of Mission 13 (2011 hours) the unit was shutdown in preparation for teardown analysis.

4.1.4.2 Results of Temperature Study

The platinum thermocouples which were installed internally in the B/U 101 stack on cell assemblies no. 3 and 4 were monitored throughout the endurance life test. The locations of these thermocouples are shown in Figure 7. Early in Mission 1, it was noted that thermocouples 4 and 7 which were located on the cathode near the coolant inlet indicated a temperature 6 to 8°F higher than indicated by the external coolant line thermocouples. This difference was noted to be nearly the same at both normal and high load operation, which

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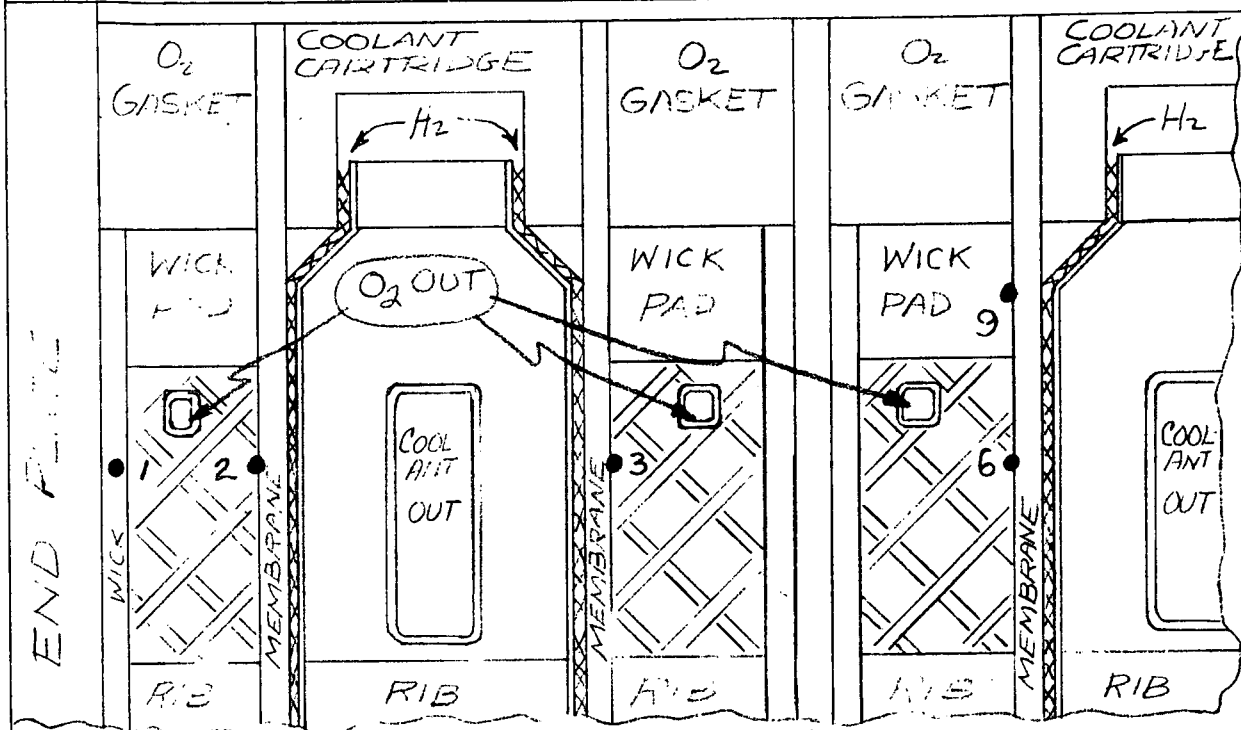
THERMOCOUPLE LOCATIONS
BUILDUP No. 101

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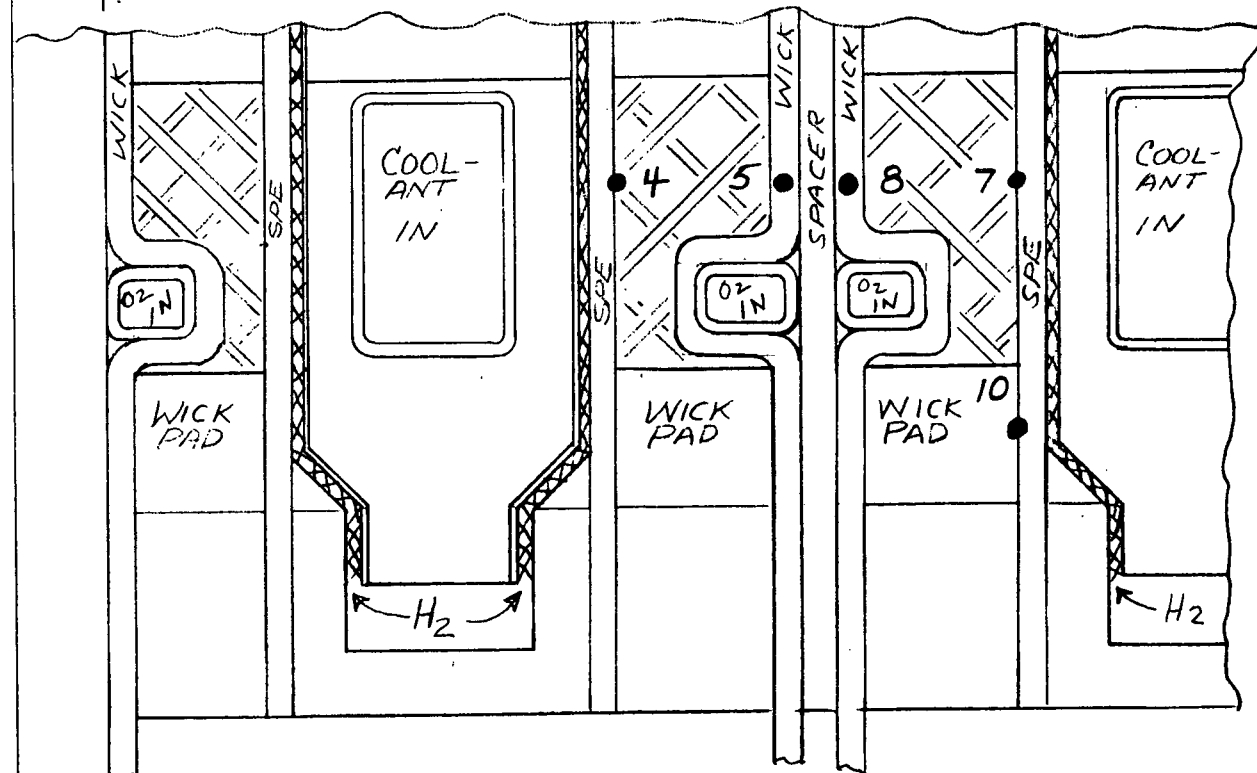
FIRST MADE FOR

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CELL No. 4

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indicated thermocouple error rather than a true high temperature area on the cathode. It was concluded that the error was probably in the external thermocouple which was mounted on the stainless steel tubing near the front panel but inside the test case. Heat was apparently being conducted along the coolant line to the front panel which was uninsulated, resulting in the error. After insulating the front panel and the coolant lines, the error was reduced to approximately 2°F.

This was no differential temperature between points 4 and 5 or 7 and 8 thus indicating that a drying condition due to water evaporation from the wicking was not present. The differential temperature between coolant inlet and coolant outlet areas of the cells were exactly as calculated.

4.1.4.3 Product Water System Performance

The product water system, which contained a water separator for each cell assembly, operated normally throughout most of the endurance life test. The water delivery rates from all separators remained equal within $\pm 2.5\%$ until the coolant pump failure which caused the shutdown at the 1634 hour point. Also prior to the shutdown, practically no water was noted to accumulate in the case. After the shutdown, the delivery rates began to fluctuate and overflow water began to accumulate in the test case. Examination of the water system valves external to the test case disclosed an accumulation of foreign material which was suspected to have restricted the flow. However, removal of this material resulted in no improvement. Later, all water separators and lines were purged by increasing the O_2 to H_2O ΔP until O_2 passed through the porous glass separators and out the water delivery lines. This resulted in additional residue coming from the separator on cell 4. After this purge however, there was still no improvement in flow characteristics and erratic operation of the water system continued until the test was terminated. Laboratory analysis of the residue from the valves showed it to be mold and gram negative non-sporulating bacteria.

The product water was analyzed to determine its potability to measure fluoride and chloride release to determine possible relationship to SPE membrane degradation.

The results of the potability analysis for contamination by chemicals and organics are summarized in Table IV. The fluoride and chloride release data are shown in Table V. The fluoride release data are shown in Table VI. The fluoride concentration was noted to slowly increase to about 6 ppm during the first 600 hours and then remain at that level until the test was terminated.



Table IV

B/U 101 Product Water Analysis

Constituent	B/U 101	B/U 101	B/U 101	B/U 101	MSC Specification
	0 - 436 Hours	460 - 1000 Hours	1018 - 1505 Hours	1553 - 2011 Hours	SD-W-0020 May 16, 1971
Total Solids	58.0 ppm	30.8 ppm	31.5 ppm	35.5 ppm	TBD but < 500 mg/l
Total Organics	23.2 ppm	13.6 ppm	8.5 ppm	9.5 ppm	TBD but < 100 mg/l
pH	3.90	3.70	3.72	3.80	6.0 to 8.0
Color Units	-	-	-	-	15 units
Odor Threshold	-	-	-	-	3 units
Conductivity (Micromhos/cm)	89	110	90	70	TBD
<u>CHEMICAL TYPE-PPM</u>					
Arsenic	-	-	-	-	-
Cadmium	< 0.01 ppm	< 0.01 ppm	< 0.010 ppm	< 0.010 ppm	0.01 mg/l
Chromium (Cr ⁺⁶)	< 0.01 ppm	< 0.01 ppm	< 0.02 ppm	< 0.02 ppm	0.05 mg/l
Copper	0.32 ppm	0.029 ppm	0.030 ppm	0.026 ppm	1.0 mg/l
Iron	0.17 ppm	0.07 ppm	0.068 ppm	0.033 ppm	0.3 mg/l
Lead	< 0.05 ppm	< 0.05 ppm	-	-	0.05 mg/l
Manganese	0.038 ppm	< 0.025 ppm	< 0.025 ppm	< 0.025 ppm	0.05 mg/l
Magnesium	0.014 ppm	0.005 ppm	0.005 ppm	0.004 ppm	0.005 mg/l
Potassium	0.42 ppm	0.13 ppm	0.07 ppm	0.06 ppm	-
Sodium	1.8 ppm	0.8 ppm	1.2 ppm	1.1 ppm	-
Sulfate	-	-	-	-	-
Cyanide	-	-	-	-	-
Fluoride	2.7 ppm	5.5 ppm	5.2 ppm	4.9 ppm	-
Titanium	< 0.2 ppm	< 0.2 ppm	< 0.2 ppm	< 0.2 ppm	-
Platinum	-	-	-	-	-
Chloride	6.3 ppm	1.9 ppm	1.5 ppm	1.1 ppm	-
Silica	80 ppm	47 ppm	86 ppm	76 ppm	-
Silver	< 0.025 ppm	< 0.025 ppm	0.025 ppm	< 0.025 ppm	0.05 mg/l
Mercury	0.22 ppm	-	< 0.025 ppm	-	-
Nickel	0.15 ppm	0.028 ppm	-	< 0.025 ppm	0.05 mg/l
Zinc	-	< 0.05 ppm	< 0.05 ppm	0.015 ppm	5.0 mg/l
<u>MICRO-ORGANISMS - COUNTS/CC</u>					
BACTERIA	-	-	300 counts/ml (24 hrs) (gram negative)	110,000 counts/ml (24 hrs) (gram negative)	Sterile
FUNGI	-	-	102,000 counts/ml (2 wks)	29,000 counts/ml (5 days)	-

Table V

B/U 101 Product Water Analysis

<u>Operating Hours</u>	<u>F⁻, ppm</u>	<u>Cl⁻, ppm</u>	<u>pH</u>
17.5	< 1	26.8	3.7
41	< 1	12.3	3.8
113	< 1	4.5	3.9
137	1.0	3.3	4.5
161	1.0	3.0	4.4
178	1.9	4.5	3.7
183	2.9	3.6	3.8
274	3.3	2.4	3.8
298	3.9	2.3	3.7
322	4.2	2.3	3.8
340	4.1	2.6	3.6
364	3.7	1.4	3.8
436	4.1	1.1	3.8
460	4.8	1.5	3.7
484	4.6	1.3	3.7
502	5.3	2.3	3.6
526	4.8	1.5	3.7
598	5.0	1.2	3.7
620	4.9	1.1	3.7
646	5.0	1.0	3.7
665	5.0	1.6	3.6
689	5.6	1.7	3.7
785	5.2	1.5	3.7
809	5.5	1.3	3.7
828	5.5	1.9	3.6
852	5.8	1.2	3.7
924	5.9	1.1	3.7
972	5.7	1.2	3.7
1000	5.4	1.5	3.7
1018	5.6	2.3	3.6
1066	5.4	1.1	3.7
1138	5.4	< 1	3.7
1181	6.2	1.2	3.7
1229	5.7	< 1	3.7
1301	5.7	< 1	3.7
1334	6.3	1.4	3.7
1391	6.3	1.1	3.7
1463	6.3	< 1	3.7
1505	6.1	1.3	3.6
1553	6.0	< 1	3.7
1625	5.2	< 1	3.7
1657	5.4	< 1	3.6
1705	5.7	< 1	3.7
1801	5.4	< 1	3.7
1866	5.3	< 1	3.8
1917	5.6	1.0	3.8
1963	5.6	1.4	4.0
2011	4.4	1.4	3.9

Table VI

B/U 101 Product Water AnalysisF⁻ Ions in ppm

<u>Operating Hours</u>	<u>Cell No. 1</u>	<u>Cell No. 2</u>	<u>Cell No. 3</u>	<u>Cell No. 4</u>	<u>Pooled</u>
17.5	<1	<1	<1	<1	<1
41	<1	<1	<1	<1	<1
113	<1	1.2	1.2	1	1
137	<1	1.3	1.5	1	1.0
161	<1	1.4	1.6	1	1.0
178	1.4	2.4	2.5	1.4	1.9
183	2.2	3.2	3.3	2.3	2.9
202	2.4	3.4	3.5	2.3	2.9
274	3.0	3.8	4.2	2.6	3.3
298	3.7	4.3	4.7	2.8	3.9
322	3.9	4.8	5.2	3.1	4.2
340	4.4	4.1	4.8	3.4	4.1
364	4.4	3.5	4.0	3.1	3.7
436	5.1	3.8	4.1	2.9	4.1
460	5.9	4.3	5.3	3.2	4.8
484	5.8	4.4	3.4	5.5	4.6
502	6.3	4.3	6.3	4.1	5.3
526	6.2	4.2	5.1	3.9	4.8
598	6.5	4.2	5.4	3.9	5.0
620	6.5	4.4	5.5	3.9	4.9
646	6.2	4.4	5.5	3.9	5.0
665	6.2	4.3	5.5	4.1	5.0
689	7.6	4.3	5.6	5.0	5.6
785	6.7	4.6	5.4	4.6	5.2
809	6.2	4.7	5.7	4.8	5.5
828	6.7	4.7	5.8	4.6	5.5
852	7.7	4.8	6.1	4.8	5.8
924	7.7	4.9	6.5	4.7	5.9
972	6.7	5.2	6.5	4.9	5.7
1000	6.5	5.0	5.9	4.7	5.4
1018	7.0	5.6	5.2	4.6	5.6
1066	7.4	4.6	5.4	5.2	5.4
1138	6.9	4.4	4.9	4.8	5.4
1181	8.1	4.9	5.1	5.5	6.2
1229	7.9	4.9	4.9	5.4	5.7
1301	7.4	5.4	5.4	5.3	5.7
1343	8.1	5.1	5.8	5.4	6.3
1391	8.2	5.0	5.6	5.7	6.3
1463	7.9	5.5	5.8	5.8	6.3
1505	7.8	5.4	5.4	5.8	6.1
1553	7.5	5.5	4.7	5.7	6.0
1625	6.9	4.8	4.5	5.1	5.2
1657	6.9	5.0	5.0	5.1	5.4
1705	5.8	5.7	6.2	4.7	5.7
1801	5.0	5.8	6.2	4.9	5.4
1866	6.0	4.3	5.2	5.4	5.3
1917	6.2	5.3	5.2	5.8	5.6
1963	6.2	5.3	5.2	5.8	5.6
2011	4.9	4.4	3.8	4.3	4.4

4.1.5 TEARDOWN ANALYSIS

Buildup 101 was disassembled for teardown analysis on 9/24/71.

4.1.5.1 Pre-Teardown Testing

Prior to removal of the stack from the test case, the following check-out tests were performed with the results as shown. Also included are comparable readings taken prior to the start of the endurance test.

1000 Hz Impedance

<u>Cell Position</u>	<u>Initial (Mission 1), ohm</u>	<u>Final (After Mission 13), ohm</u>
1	.00116	.00125
2	.00108	.00112
3	.00110	.00116
4	.00110	.00112
Total	.0041	.0046

60 Hz Impedance

	<u>Initial</u>	<u>Final</u>
1	.0026	.0027
2	.0019	.0025
3	.0019	.0025
4	.0023	.0024
.Total	.0087	.0100

Helium Diffusion Test at 3 psid

	<u>Before Test (5/27/71), cc/hr</u>	<u>After Test (9/24/71), cc/hr</u>
O ₂ to H ₂ System	31.8	47.6
O ₂ to Coolant System	0	0
O ₂ to Water System #1	2.4	0
O ₂ to Water System #2	2.4	1.2
O ₂ to Water System #3	6.0	2.4
O ₂ to Water System #4	2.4	0

4.1.5.2 Teardown Observations

The test case cylinder was removed to allow close examination of the wiring, piping and water system. The following observations were made:

- 1) All components appeared to be in good condition.
- 2) White particles noted on inside of water separators. These were apparently glass particles which had loosened from the inside surface of the porous separator.
- 3) No discoloration of the glass separators or the Dacron wick was noted.
- 4) Nylon insulating washers at ends of tie rods badly oxidized. However, they had not shorted to end plate spacing.

A vacuum leak test on the H₂ system with the piping of the front panel intact indicated a leak rate of 93.3 cc/hr at a ΔP of 26.8 inches Hg. This is approximately three times normal leakage. This test was repeated on the stack alone with the H₂ lines removed and with nearly the same results.

Prior to the teardown of the stack, a series of tests was performed on the water system to attempt to determine the reason for its erratic performance after the coolant system failure.

The water separators were first removed from the cell wicks. Separator no. 4 was placed into a sterilized container and held for lab analysis for bacteria and fungus contamination. Separator no. 2 broke when it was being removed. Separators 1 and 3 were leak and flow tested with the following results compared with pre-test performance:

<u>Separator No.</u>	<u>cc/min Flow at $\Delta P = 7''$ Hg</u>		<u>Bubble Point, inches Hg</u>	
	<u>Pre-Test</u>	<u>Post-Test</u>	<u>Pre-Test</u>	<u>Post-Test</u>
1	150	300	13	16
3	20	37.5	14.5	14

Separator no. 1 was then flow tested with a new wick clamped with wick clip no. 1. Operation was normal. These tests indicated no abnormal operation of either the water separators or the interface between the separators and the wicks.

Tests were then performed to determine whether one or more of the stack wicks was restricted. With the stack in the normal operational attitude and the water separators removed, water was slowly introduced into the O₂ side through the O₂ purge line. After adding a total of 40 cc, water was noted to be dripping from the cell 2 wicks. The wicks on the other cells felt wet but were not saturated.

Water separator no. 3 was then installed on cell no. 3 and a normal ΔP of 7 inches Hg applied by vacuum pump on the water side. A flow rate of .375 cc/min was obtained. This rate exceeds the average product water flow during fuel cell operation. Similar tests on the other cell wicks indicated that the wicks were apparently operating normally under these conditions.

4.1.5.3 Stack Tests and Teardown Observations

Prior to the teardown of the stack, tests were performed to determine the effect of increased or decreased end plate compression on the H₂ side leak rate. Tests would indicate possible gasket seal leakage. Vacuum leak tests were performed after tightening the tie rods and nuts 1 1/4 turns. The leakage rate was decreased slightly from 93.3 to 68.4 cc/hr. Leakage checks were then run with loosened tie rods with the following results:

<u>Tie Rod Tightness</u>	<u>Leakage Rate, cc/hr</u>
Back to original	84
1 turn loose	84
2 turns loose	88.8
3 turns loose	87.6
4 turns loose	90

These results indicated that the gasket manifold seals were not contributing to the H₂ system leakage.

The stack was then disassembled and the following observations were noted:

- 1) Product water wicking appeared clean and normal.
- 2) H₂ humidification pads appeared dry and would not readily rewet without rubbing water into them.

- 3) Membrane bond areas on all cells were blistered at the top and bottom over the H₂ inlet channels.
- 4) Discoloration of the O₂ gaskets adjacent in the area where the wicks cross at the bottom edge. Some curling of the gaskets also noted in this area.
- 5) Cathode LNP surface uniform in color and appeared like new. It was uniformly covered with droplets of water.

A vacuum leak test on the H₂ side of Cell 4 (SN 24) disclosed a leak rate of 90 cc/hr which was nearly the same rate obtained on the stack. A positive pressure check at 40 inches H₂O helium pressure disclosed a membrane/frame bond leak at the top H₂ channel toward the H₂ inlet manifold. The membrane bond was blistered at the point of leakage.

Additional vacuum leak tests were performed on Cell 4 (SN 24). During these tests each edge of the cell was immersed in water to determine whether or not other bond leakage existed. The results indicated leakage at the bottom edge also.

The cell was then clamped between two pedigree fixture end plates which applied uniform gasket loading to the membrane bond areas. A vacuum leak test was performed which indicated normal membrane diffusion rate of 9.3 cc/hr. Thus, no cross-membrane leakage was identified in Cell 4 (SN 26).

An O₂-to-H₂ side vacuum leak test on the remaining three cells assembled into a 3-cell stack indicated a normal diffusion rate of 24 cc/hr.

Cell 4 (SN 26) was sent to lab for stripping and further analysis, the results of which are given in section 4.1.5.4.

4.1.5.4 B/U 101, Cell No. 4 Analysis

After successful completion of 2000 hours of operation, B/U 101, Cell No. 4 was released to the laboratory for analysis. The cell was sectioned and subjected to the following physical and chemical analyses:

- A. Delamination Inspection/Microtome.
- B. Bond Strength Evaluation.
- C. Tensile, Elongation/Delamination.



- D. Water Content/Delamination.
- E. 3 x 3 Inch Performance.
- F. IR Cesium Form Evaluation/Delamination.
- G. Contamination Analysis/Delamination.
- H. Water and Gas Permeability.
- I. Visual Examination After Platinization.
- J. Degradation Test ($\text{H}_2\text{O}_2/\text{Fe}^{+2}$).

The resulting data showed no membrane delamination, poor bond strength, comparable degradation (as indicated by infrared CO/CF) throughout membrane, no inhibiting membrane contamination, no gross porosity increase in membrane, lowered membrane tensile and elongation, similarity in platinization properties between new and used (2000 hr) membrane and an increase in the iron-peroxide induced fluoride release of the used membrane.

Analytical Results

Delamination/Microtome

No delamination was observed in any of the decatalyzed membrane. Particular note was made of the usual problem areas around the gas inlets, and no delamination was found. Cross-sectional areas of membrane were examined microscopically, and a discoloration which progresses through the membrane from the anode side was noted. The same type of stain was observed at the H_2 inlet of Cell 163-L. This "stain" is resistant to aqua regia and, therefore, probably not a metallic material.

Bond Strength - Table VII

The bond areas 90° from the bus bar edge showed a poor to non-existent bond between the "R" membrane and polysulfone. Blisters were apparent, and further examination showed strength in these areas only at the flash. The gold-to-polysulfone and the gold-to-"R" membrane bonds along the bus bar edges were non-existent and the materials could be easily separated. The "R"-to-polysulfone and niobium-to-polysulfone bonds were pulled on the Instron and these values are tabulated in Table VII.

Table VII

Bond Strength Evaluation - Bonded Areas SS B/U 101, Cell No. 4

Sample Identification	Bond Strength, lb/in.				
	Au/PS	"R"/PS*	"R"/Au	Nb/PS	
				Outside**	Inside** Peak/Peel
B 2-8/ 2	0	--	0	0	---/---
3	0	4.6	0	0	2.0/1.0
4	0	5.9	0	0	> 4/0.8
5	0	6.8	0	0	1.5/0.8
6	0	4.2	0	0	1.5/0.6
7	0	8.1	0	0	---/---
8	0	3.4***	0	0	6.2/0.9
9	0	--	0	0	0/0
10	0	--	0	0	0/0
B 1-5		0			
B 4-6/ 1	0	6.7	0	0	7/5.6
2	0	13.1	0	0	14/2.4
3	0	12.8	0	0	10/3.5
4	0	9.4	0	0	> 8/3.5
5	0	12.9	0	0	10/1.0
6	0	7.8	0	0	11/1.6
7	0	--	0	0	10/0.9
8	0	14.4	0	0	6.3/3.3

* Membrane tore - bond strength > recorded value.

** Outside polysulfone is against "R" membrane; inside polysulfone is against polysulfone. These two polysulfone frames sandwich the niobium.

*** Membrane did not break, actual bond peel.

Tensile and Elongation - Table VIII

The tensile and elongation values obtained for the used membrane sections are lower than those reported for the incoming membrane. However, the discrepancy between the new and used tensile values may not be 1000 psi as the reported values would indicate. All incoming membrane testing is done after a 100°C water equilibration; whereas, the B/U 101 membranes were autoclaved prior to M and E assembly. Also, the tensile values for the used membrane were based on a measured thickness which could not account for screen indentation. The unused membrane tensile values may be higher than corresponding B/U 101 autoclaved values would be, and the B/U 101 membrane tensile values reported may be lower than the actual values should be because of screen indentations. No membrane delamination was observed.

Water Content - Table IX

Water content measurements were made on five sections of membrane from the edge toward the center. The section of membrane closest to the bonded edge shows water content slightly lower than the adjacent sections which show standard autoclave water contents. This edge drying, although real, was probably not of impairing magnitude.

3 x 3 Inch PerformanceCesium Form IR Spectra - Table X

Cesium form infrared spectra were obtained on hydrogen inlet, oxygen inlet and center membrane sections. The CO/CF values were comparable for all four membrane areas. The CH/CF values at the O₂ inlets were 10 times those at the H₂ inlet and the center. More laboratory data is necessary before a correlation between CO/CF or CH/CF and degree of membrane degradation can be made. The CO/CF ratio indicated that the degree of degradation of the membrane from Cell No. 4 was uniform over the entire membrane.

Contamination - Table XI

An analysis for contaminants of three membrane areas showed no gross contamination of the membrane. The source of the contaminants found is most likely glass or some similar material as indicated by Na⁺, Mg⁺⁺, etc. The level of contamination found was low and would not inhibit membrane function.

Water and Gas Permeabilities - Table XII

The water and gas permeabilities for the O₂ inlet areas showed no gross porosity increase in the membrane in the wet and dry mode, respectively. Values were comparable to those previously reported for unused membrane.

Table VIII

Tensile and Elongation, SS B/U 101, Cell No. 4

<u>Sample Identification</u>	<u>Tensile, psi*</u>	<u>Elongation, %</u>
C-1	2486	168
C-2	2570	144
C-3	2735	150
C-4	2388	148
C-5	2498	158
C-6	2344	140
C-7	2267	128
C-8	2065	120

* Values reported were calculated using a measured thickness which does not account for screen depressions.

Table IX

Water Content Measurements, SS B/U 101, Cell No. 4

<u>Sample Identification</u>	<u>% H₂O*</u> <u>(as taken from cell)</u>
D-1 Edge 1/4 inch	29
D-2 Adjacent 1/4 inch	33
D-3 Adjacent 1/4 inch	36
D-4 Adjacent 1/4 inch	34
D-5 Adjacent 1/2 inch	35

* $\frac{\text{Wet Wgt} - \text{Dry Wgt}}{\text{Dry Wgt}} \times 100 = \% \text{ H}_2\text{O}.$

Table X

Cesium Form IR Spectra, SS B/U 101, Cell No. 4

<u>Sample Identification</u>	<u>C-H/C-F</u>	<u>C=O/CF</u>
F-1 (H ₂ Inlet)	0.004	0.01
F-2 (Center)	0.005	0.03
I-1 (O ₂ Inlet)	0.05	0.02
I-2 (O ₂ Inlet)	0.05	0.02

Table XI

Cation IEM Contamination Analysis, SS B/U 101, Cell No. 4

<u>Sample Identification</u>	<u>Cation Contaminant</u>					<u>Na</u>
	<u>Ca</u>	<u>Co</u>	<u>Fe</u> <u>μg/cm² IEM</u>	<u>K</u>	<u>Mg</u>	
H-1	3	< 2	< 3	4	1.5	5.5
H-2	3	< 2	< 3	1	2	1
H-3	3	< 2	< 3	5	1	7

Membrane Platinization

Two sections of used membrane from Cell No. 4 were processed by the standard platinization procedure. The resulting platinized membrane sections were black and opaque; and when a cross section was examined under a microscope, the characteristic center non-platinized section was seen.

Degradation Testing (H_2O_2 - Fe^{+2}) - Table XIII

A standard peroxide/iron degradation test performed on a section of Cell No. 4 resulted in a mg F^-/g IEM twice the allowable limit for incoming membrane. This may indicate an increase in susceptibility of the B/U 101 membrane to peroxide/iron attack. The presence of C=O and C-H groups after 2000 operations is probably what is causing the increase in degradation rate.

Table XII

Permeabilities - Gas and Water at Oxygen Inlets

SS B/U 101, Cell No. 4

<u>Sample</u>	<u>Permeability</u>	
	<u>O₂</u>	<u>H₂O</u>
	<u>cm²/atm sec x 10⁻⁸</u>	
I-1	1.9	3.6
I-2	2.8	3.6

Table XIII

Peroxide Degradation

<u>Sample</u>	
<u>Identification</u>	<u>mg F⁻/g Membrane</u>
K-1	2.8
K-2	Sample to small

4.1.6

CONCLUSIONS AND ACTIONS

The following conclusions can be drawn from the analysis of the endurance life test data and the evaluation of the teardown observations and laboratory analyses:

- 1) The design modifications introduced in B/U 101 and the changes made in the test operating conditions appear to have corrected the membrane degradation failure mode experienced in previous buildups.
- 2) The results of the temperature study showed that previous buildups had apparently been operated with a coolant inlet temperature of approximately 6°F higher than recorded.
- 3) The performance of the product water removal system was satisfactory until it was adversely affected by a unit shutdown (water valve open) which apparently caused loss of prime in the wicks.
- 4) The membrane bonding system appears to be marginal for 2000 hours life when unsupported. However, the minor leakage experienced in one cell did not adversely affect the performance of the unit.
- 5) The total hydrogen fluoride released during the 2000 hour test apparently is not related to membrane delamination/degradation at the gas inlets.

Based upon the above conclusions, the following actions will be undertaken:

- 1) Introduce modifications to the stack design to provide increased O₂ gasket loading against the membrane bond areas to improve bond life. Verify this fix by introducing it into a rebuilt Buildup 101A with the three remaining cells from B/U 101. This buildup will be operated at the same conditions as B/U 101.
- 2) Modify the test facilities to provide automatic shutoff of the product water valve when an automatic unit shutdown occurs.
- 3) Continue to evaluate design and operational modifications in laboratory 3 x 3 inch fixtures.
- 4) Evaluate more simplified stop/start procedures during the operation of B/U 101A.

4.2 Fabrication and Test of B/U 102

A complete report of the fabrication, testing and failure analyses of this unit is contained in SPR-054, Component Test and Evaluation Report, Small Stack B/U 102.

4.2.1 Summary

As a continuation of the evaluation of the modified design introduced in B/U 101, Buildup 102 was fabricated for endurance life testing without prehumidification of the hydrogen reactant.

The design of B/U 102 was the same as B/U 101 with the following exceptions:

- . The cathode catalyst was eliminated from under the H₂ humidification wick pads to allow greater water transport rate to the membrane and reduce H₂O₂ generation in the H₂ inlet area.
- . A single water separator of the EM-1 design was used.
- . No internal thermocouples were installed in the stack.

B/U 102 was fabricated during July 1971 and delivered to test on 7/13/71, the test conditions being 45 psia O₂ pressure and 150°F coolant inlet temperature. Unlike B/U 101, B/U 102 used prehumidification of only the inlet oxygen. Humidification of the H₂ depended solely upon the H₂ humidification wick pads installed at each cell H₂ inlet area. The cell performance, although initially low, became equivalent to B/U 101 after four electrolysis activations during Mission 1 and activation for Mission 2.

The mission cycle life test continued satisfactorily into the sixth mission when, at the 915 hour point, a facility power failure caused the automatic shutdown of the unit. It was restarted without difficulty. Then at the 1092 hour point, the main hydrogen facility solenoid shut-off valve failed closed, again resulting in the automatic shutdown of the buildup. Following these shutdowns, the product water delivery rate from the separator was noted to be considerably reduced with overflow occurring into the test case. This same condition was observed on B/U 101. Performance of the cells was not adversely affected, and the life test was continued. Various corrective procedures were attempted on the B/U 102 water system, resulting in satisfactory operation of the separator after reverse flushing and cleaning the external valving. However, certain cells remained purge sensitive from that time until failure. The test continued until the 1762 hour point when a rapid decay in the voltage of Cell No. 1 and a later high O₂-to-H₂ leak rate indicated unit failure.

Teardown disclosed a membrane leak at the top edge at the H₂ inlet manifold of Cell 1. Membrane delamination/degradation had occurred only at the top H₂ inlet channels of all cells examined. It was postulated that the top H₂ humidification wick pads had not provided sufficient recycle water after the loss of wick prime occurred during Mission 6. Various component tests were then performed on simulated water removal systems with results that support this postulation.

Corrective action will be to modify the test facility so that the product water valve will close whenever an automatic shutdown occurs.

4.2.2 DESIGN

The design of B/U 102 was identical to B/U 101 except for the changes discussed in section

4.2.2.1 Membrane/Electrode Configuration

The characteristics of the membrane/electrode assemblies are listed below:

- 1) No platinum catalyst in the membrane.
- 2) Anode loading 30 mg/cm².
- 3) Cathode loading 7 to 8 mg/cm².
- 4) AF-42 prebonded to anode bus bars.
- 5) Membrane water content 35 to 40 wt %.
- 6) Cut back LNP wetproofing and catalyst in area of H₂ humidification pads.

4.2.2.2 Cell Assembly Configuration

The configuration of the cell assembly had the following features:

- 1) Compartmentalized H₂ cavity.
- 2) Two H₂ inlet manifolds and channels.
- 3) Catalytic scavengers in H₂ inlets.

4.2.2.3 Oxygen System Configuration

The design of the oxygen system consisted of the following:

- 1) H₂ humidification pads at top and bottom edges.
- 2) Short O₂ inlet tubes.
- 3) Single layer of product water wicking of the EM-1 design with wider portion extending from stack.
- 4) Redesigned O₂ tube guard at inlet and purge tubes.

4.2.2.4 Stack Assembly

The configuration of the B/U 102 stack assembly was the base line design except for the water system which was the EM-1 design. No internal thermocouples were installed as in B/U 101.

4.2.3 Fabrication

B/U 102 was fabricated during July 1971. The same procedures were used to fabricate membrane/electrodes and cell assemblies as in B/U 101.

After mounting and piping the stack to the test case front panel, vacuum leakage tests were performed which showed the coolant system to be leaktight at 10.5 in. Hg vacuum. The stack hydrogen system leak rate was 31.87 cc/hr at 25 to 28 in. Hg vacuum. This is considered normal diffusion for a 4-cell assembly stack.

Buildup 102 was completed and shipped to test on 7/12/71.

4.2.4 ENDURANCE TEST HISTORY

The Buildup 102 test configuration in test stand station 2 is shown in Figure 8. A gas humidifier was used to saturate inlet oxygen. Preliminary leakage tests performed prior to activation indicated normal diffusion rates at mission pressure conditions. The results are as follows:

B/U 102 was activated on 8/14/71, but a low voltage setting on the power supply during the initial electrolysis resulted in a procedural deviation from standard activation procedures. A comparison is given below:

<u>Normal Procedure</u>	<u>B/U 102 Procedure</u>
1. Short electrolysis - 2 to 3 minutes	1. 10 minute/10 amp electrolysis
2. Deep discharge	2. Deep discharge
3. 10 minute/10 amp electrolysis	3. Short electrolysis - 2 to 3 minutes

The initial performance of Cells 1 and 3 over the first 19 hours was lower than normal, so a third electrolysis of 35 amps for 10 minutes was performed. The performance of Cells 1 and 3 increased but was still below normal at 42 load hours. Frequent oxygen purging was required during this period with a 10-second purge every 10 minutes providing adequate operation.

At the 42 hour load point, a fourth electrolysis of 35 amps for 25 minutes was performed which successfully raised the performance levels of all cells to normal. At the 120 hour load point, a 5-second purge every hour was established and maintained throughout all steady state endurance testing with normal performance.

During Mission 1, after the fourth electrolysis, individual cell performance ranged from .805 to .823 volt. These levels steadily improved at each mission until an .835 to .841 volt range was achieved during Mission 13. These levels are higher than B/U 101 and virtually all previous buildups except B/U 4 which was at about the same level.

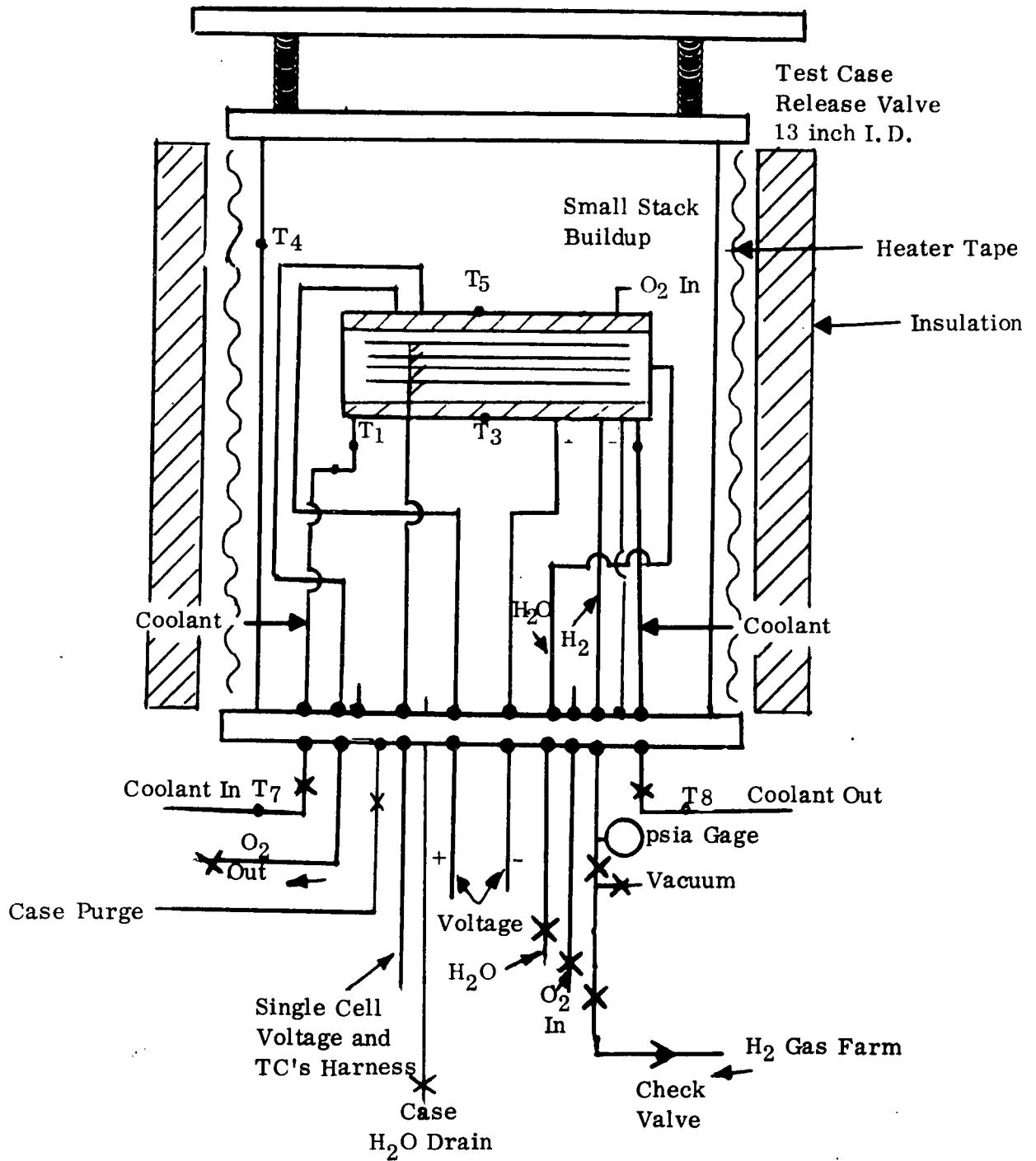


Figure 8. Buildup 102 Test Configuration

Figure 9 is a chronological plot of buildup voltage and current vs. time for the 13 missions (1762 operational hours). Steady state operating conditions were:

45 psia - oxygen
41 psia - hydrogen
150°F - coolant inlet temperature

Figure 10 shows the approximate power profile for a mission cycle.

Product water samples were taken periodically for chemical and bacteriological analysis. Table XIV summarizes the potability analysis for contamination by chemicals and organics. Fluoride and chloride release data are given in Table XV.

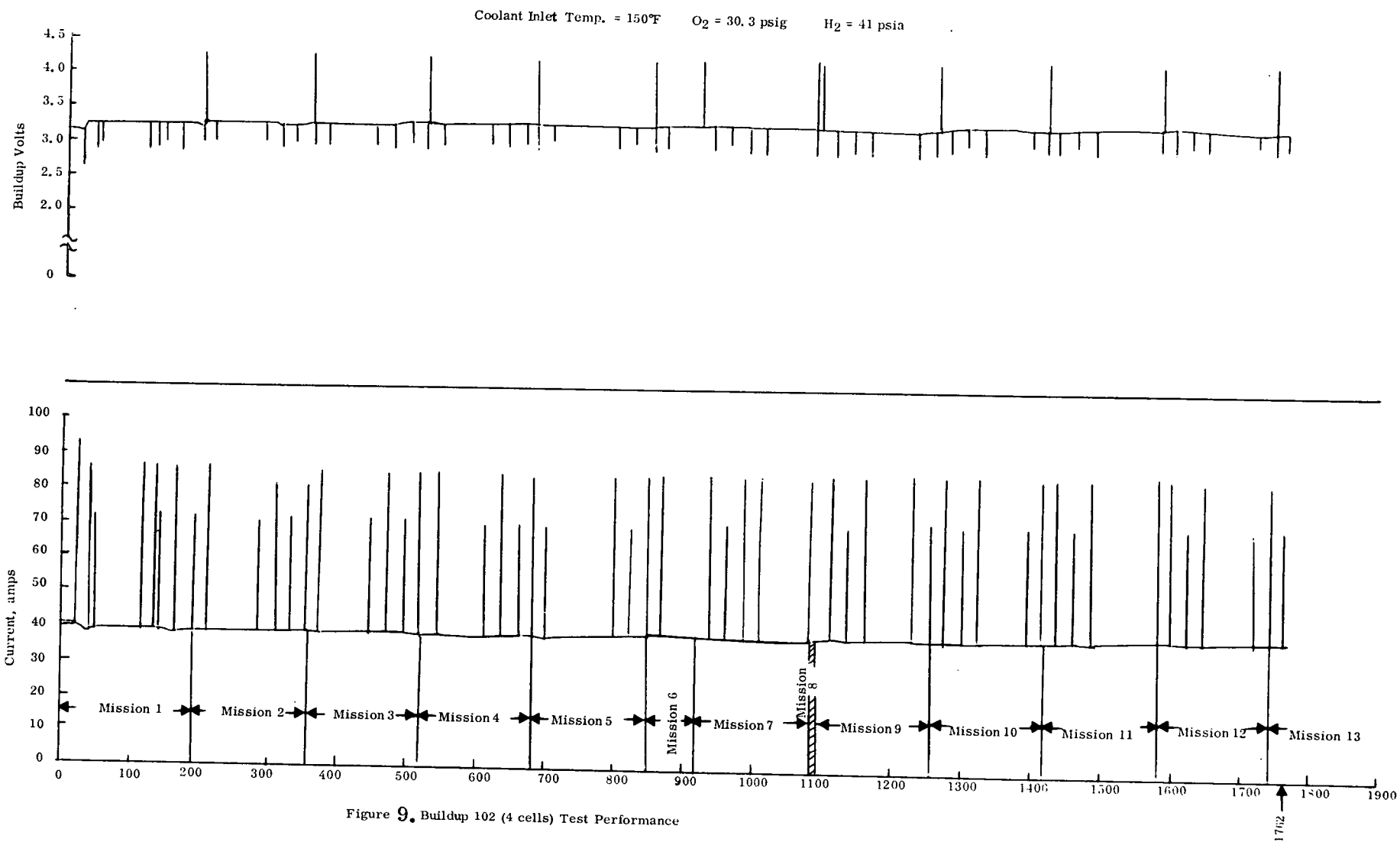
The life test continued without problems through 470 hours when a power supply fuse blew due to an excessive power demand by the simultaneous operation of several units at high loads. This resulted in a rerun of the 250 watt load point for that day.

On 9/12/71 (915 load hours) a plant-wide power failure shutdown the entire test facility. Reactivation of B/U 102 occurred on 9/13/71 and testing continued normal until 9/15/71 when a single occasion of excess case water suggested the possibility of a product water removal problem.

On 9/21/71 (1092 load hours) another automatic shutdown of B/U 102 occurred when a H₂ solenoid valve sustained a coil burn-out and shut off the hydrogen supply. Reactivation took place about 7 hours later and the unit soon developed an excessive single cell purge sensitivity that shifted from cell to cell in an erratic manner.

Subsequent operation over the next 700 hours on the same gas sources eliminated the oxygen and hydrogen as the source(s) of the purge sensitivity. The product water delivery rate through the separator was severely reduced during Mission 9 operating following the solenoid valve failure. The facility product water piping and valving was flushed and found to contain large amounts of bacterial growth and the separator was back-flushed with 500 cc of distilled water. Later, one of the product water removal valves was discovered to be plugged up and was bypassed until a change of valves could be made at Mission 10 completion. Following these actions, water removal returned to normal.

Performance continued at high levels with periods of single cell purge sensitivity varying from normal to greater-than-normal amounts for the balance of life testing.



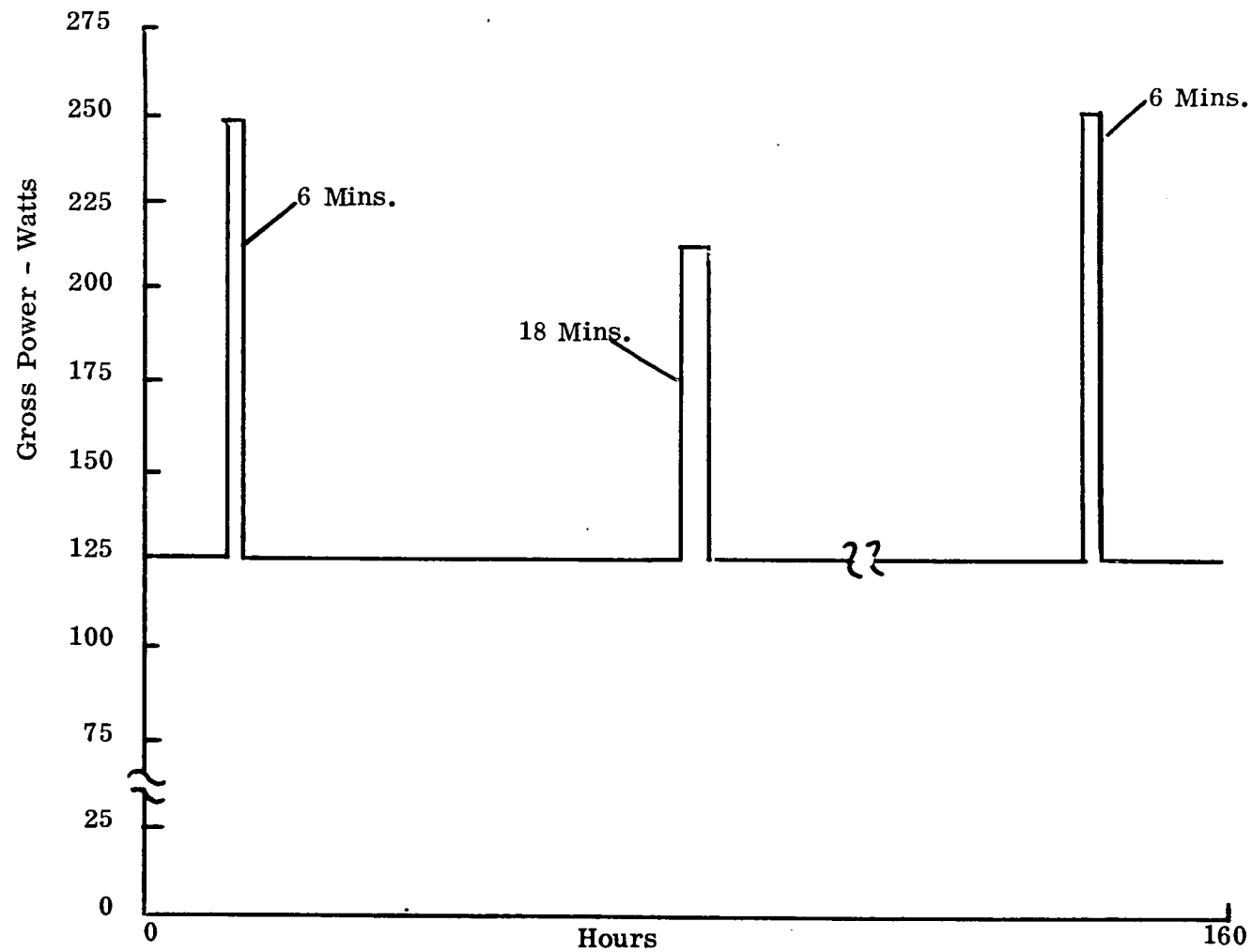


Figure 10. Mission Cycle Power Profile

Table XIV

B/U 102 Product Water Analysis

Constituent	Space Shuttle B/U 102 42-494 Hours	Space Shuttle B/U 102 538-1008 Hours	MSC Spec. SD-W-0020 May 16, 1970
Total Solids	40.5 ppm	29.0 ppm	TBD but <500 mg/l
Total Organics	13.5 ppm	7.0 ppm	TBD but < 100 mg/l
pH	3.72	3.67	6.0 to 8.0
Color Units			15 units
Odor Threshold			3 units
Conductivity (Micromhos/cm)	90	105	TBD

CHEMICAL TYPE-PPM

Arsenic			-
Cadmium	< 0.01 ppm	< 0.01 ppm	0.01 mg/l
Chromium (Cr+6)	< 0.02 ppm	< 0.02 ppm	0.05 mg/l
Copper	0.035 ppm	0.013 ppm	1.0 mg/l
Iron	0.05 ppm	0.02 ppm	0.3 mg/l
Lead			0.05 mg/l
Manganese	< 0.025 ppm	< 0.025 ppm	0.05 mg/l
Magnesium	0.014 ppm	0.005 ppm	0.005 mg/l
Potassium	0.32 ppm	0.19 ppm	-
Sodium	0.8 ppm	1.1 ppm	-
Sulfate			-
Cyanide			-
Fluoride	4.6 ppm	5.8 ppm	-
Titanium	< 0.2 ppm	< 0.3 ppm	-
Platinum			-
Chloride	1.7 ppm	1.3 ppm	-
Silica	86 ppm	47 ppm	-
Silver	< 0.025 ppm	< 0.025 ppm	0.05 mg/l
Mercury			-
Nickel	< 0.025 ppm	< 0.025 ppm	0.05 mg/l
Zinc	< 0.05 ppm	< 0.05 ppm	5.0 mg/l

MICRO-ORGANISMS - COUNTS/CC

BACTERIA

5600 counts/ml (24 hrs)

Sterile

FUNGI

400 counts/ml (2 weeks)

Table XV

B/U 102 Product Water Analysis

<u>Operating Hours</u>	<u>F⁻ (ppm)</u>	<u>Cl⁻ (ppm)</u>	<u>pH</u>
42	1.0	6.7	4.3
114	3.2	3.5	3.8
138	4.6	1.8	3.8
162	4.9	1.7	3.7
186	5.2	1.5	3.7
211	4.6	2.0	3.6
283	5.2	1.5	3.7
331	5.3	< 1	3.7
374	6.2	1.2	3.5
446	6.5	1.2	3.6
494	6.0	1.3	3.6
538	6.0	1.6	3.5
610	5.7	1.3	3.7
658	5.4	1.2	3.7
701	6.9	1.4	3.6
797	6.0	1.1	3.7
864	5.6	1.3	3.6
915	6.2	< 1	3.7
960	6.2	< 1	3.7
1008	5.8	1.2	3.7
1080	6.1	1.0	3.7
1154	5.8	< 1	3.7
1231	6.2	< 1	3.8
1322	6.2	< 1	3.6
1394	5.7	< 1	3.7
1485	6.2	< 1	3.6
1581	6.5	< 1	3.6
1647	6.2	< 1	3.6
1719	6.4	1.0	3.6
1762	6.1	1.1	3.6



At 1762 hours on 10/20/71, about two minutes after setting the scheduled 215 watt load point, Cell 1 initiated a sudden voltage decay and a low voltage shutdown (automatic) occurred. Oxygen-to-hydrogen differential pressure equalized. An O₂-to-H₂ leak rate of 600 cc/min at 30 psid (oxygen) was measured, indicating excessive leakage.

There was no indication of an increased discharge rate of any cell during the period of O₂ takeover between Mission 12 completion and Mission 13 start-up (i.e., last mission change before failure).

4.2.5 TEARDOWN ANALYSIS4.2.5.1 Teardown Observations

Buildup 102 was removed from test for failure analysis on 10/20/71. Prior to disassembly, a 60 Hz impedance test indicated the following:

<u>Cell Position</u>	<u>Pre-Test Impedance, ohm</u>	<u>Post-Failure Impedance, ohm</u>
1	.0027	.0026
2	.0022	.0025
3	.0021	.0024
4	.0027	.0023

After removing the test case cylinder, it was noted that the external appearance of all components was normal. No discoloration of the water separator or wicking was noted. As in B/U 101, the nylon tie rod washers were cracked and badly oxidized. A vacuum leak test on the H₂ system with piping removed from the stack to the front panel indicated a leakage rate of over 1000 cc/hr. This leak test was repeated after tightening the stack tie rods a half-turn but no effect was seen on the leakage rate.

Upon disassembly of the stack, charred material was noted in both H₂ inlet manifolds. All cell H₂ inlet manifold tabs were deformed to the shape of the mating silicone rubber gaskets, indicating temperatures in excess of 350°F had existed. Cell Position 1 (S/N 29) was removed and a vacuum leak test performed on its H₂ compartment, disclosing a leak rate equal to that of the stack.

A positive pressure leak test was then performed on this cell with the compartment pressurized with helium at 10 inches H₂O, and the membranes supported. Through-membrane leakage was noted at a point near the H₂ manifold at the top of the inside membrane/electrode assembly (SS 81).

To determine whether bond leakage was present, the cell assembly was again vacuum leak tested at 28 inches Hg. While the vacuum was applied to the cell, water was added to the leaking area of the membrane along the H₂ inlet channel. The leak rate immediately decreased to 12 cc/hr. Apparently, no bond leakage was present.

Examination of the membrane-to-cell frame bond areas showed some blistering of the bonds. However, the blistering was not as severe as was noted during the teardown analysis of B/U 101. Cell assemblies 1 and 2 were sent to the laboratory for stripping and further analysis. These results are given in section 4.2.5.3.



Standard leak and flow tests were performed on the water separator with the following results:

Flow at $\Delta P = 7$ in. Hg, cc/min		Bubble Point, inches Hg	
<u>Pre-Test</u>	<u>Post-Test</u>	<u>Pre-Test</u>	<u>Post-Test</u>
100	162	Not tested	16

The separator showed no evidence of blockage or bacterial growth.

The product water wicking and H₂ humidification pads were tested for wettability by applying droplets of water to their surfaces. Neither would readily absorb water. However, they would become wet if the water were rubbed into their surfaces. Suspecting that the wicking had become dry during the unscheduled shutdown, a simulated water removal system was set up and tested using a cell wick pad and water separator from B/U 102. The set up is shown in Figure 11. The entire system was enclosed to prevent evaporation from the wick surfaces.

It was found that the system would not operate unless the wick was first saturated with water. The flow rate then established became 0.2 cc/min at a ΔP of 7.3 inches Hg. The top edge of the wick was then removed from the water and the separator ΔP maintained overnight (16 hours). After this simulated shutdown period, flow could not be re-established by placing the top edge of the wick in the water. The entire wick had to be rewetted.

This test was then repeated for a 2-hour shutdown period, after which startup was accomplished by merely placing the top edge of the wick into the water. The tests were continued with the evaluation of the following:

- 1) 7 hour shutdown with normal startup.
- 2) 88 hour steady state operation followed by a reverse flush of the separator to determine its effect upon flow rate.
- 3) Complete saturation of system to determine effect upon flow rate.
- 4) 24 hour shutdown with reverse flush startup.

This series of tests is summarized in the chronological plot of water flow vs. time presented in Figure 12. The results indicate the following conclusions:

- 1) Introducing water at upper end of wick will not reactivate the system after a prolonged shutdown of 16 hours.

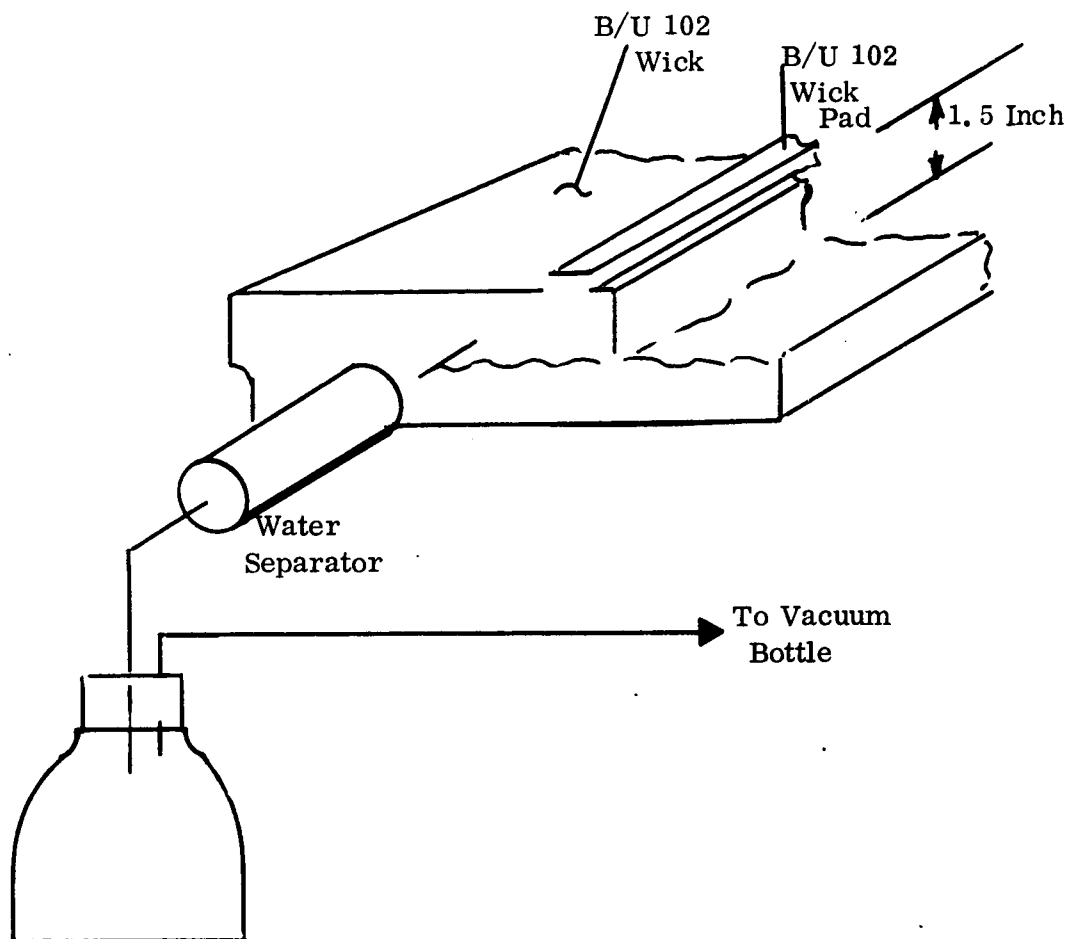


Figure 11. Simulated Water System Test Setup

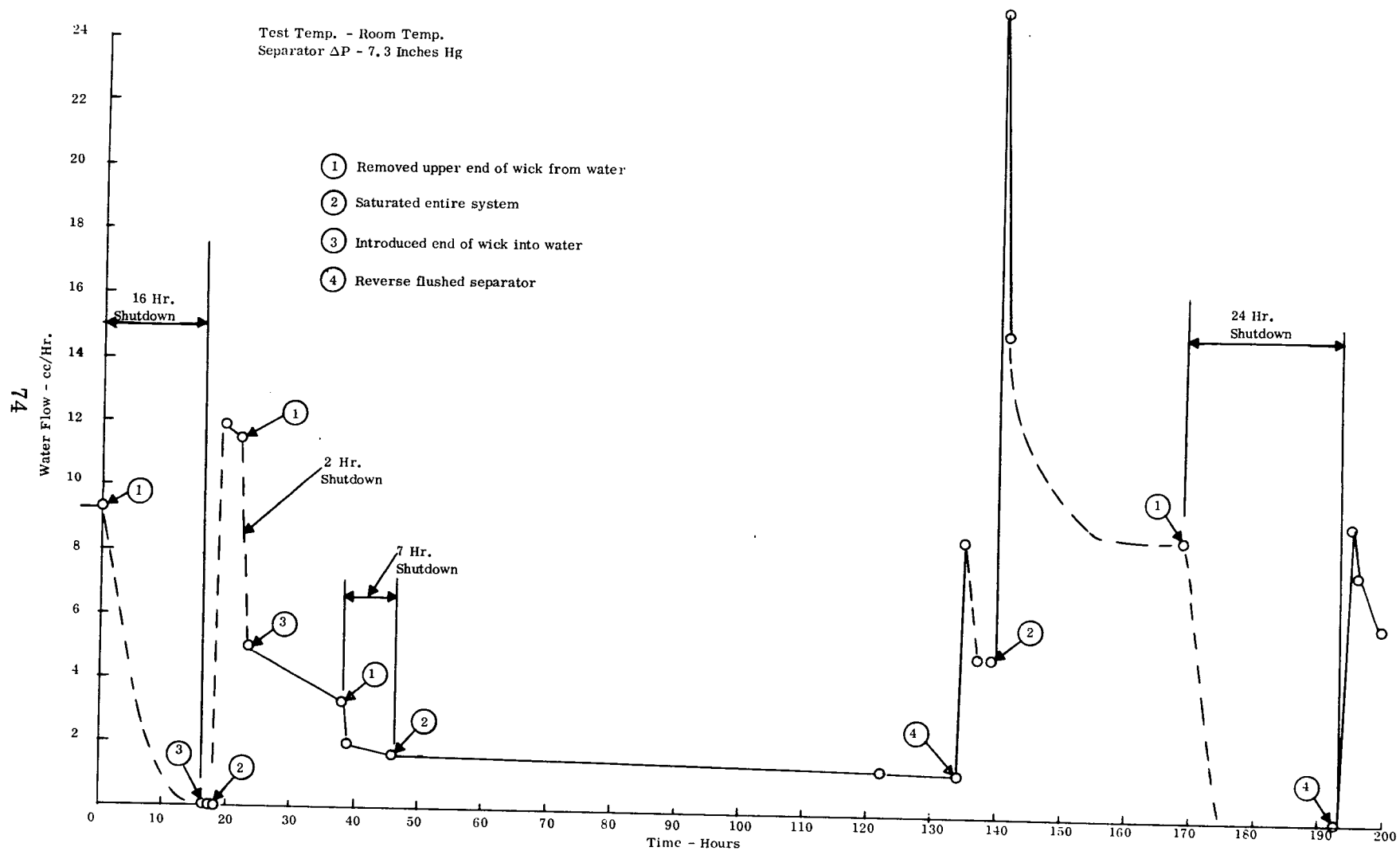


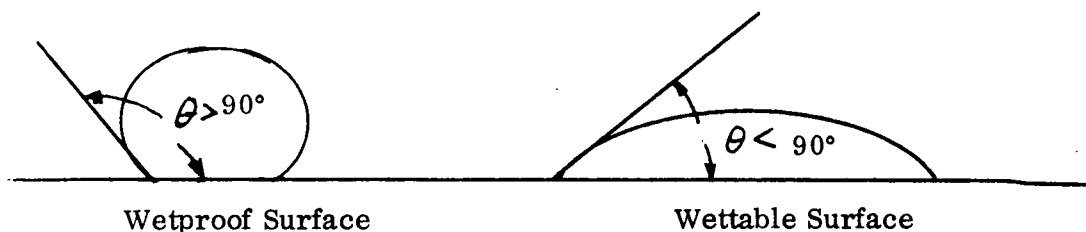
Figure 12. Test Results - Simulated Water System Space Shuttle Fuel Cell

- 2) After short shutdown of up to 7 hours, system can be reactivated by introducing water at upper end of wick.
- 3) Flow rate is reduced by a shutdown even after successful reactivation without reverse flush.
- 4) Reverse flushing improves flow rate for short term.
- 5) Reverse flushing will reactivate a system after a 24 hour shutdown.

A possible theoretical explanation for these results is given in section 4.2.5.2.

4.2.5.2 Water System Operation

A woven Dacron multifilament material is used to transport the generated product water from the cathode surface of each fuel cell to the porous water separator tube. Both Dacron and Mylar are polyesters having identical chemical composition (polyethylene terephthalate). Mylar is cited for comparison since the wetproofing characteristics of the sheet form of this material is generally better known. The surface of a material is considered wetproof if contact angle θ between a water droplet and the surface is greater than 90° (i.e., the familiar shape of a mercury droplet on a surface). The surface of a material is considered wettable if the contact angle is less than 90° (see sketch below).



If a wettable substance is used to manufacture a porous (fabric) material, water will readily be absorbed into the porous material. If a wetproof substance is used to manufacture a porous material, pressure must be used to force the water into the interstices or pores of the material. A porous material which is easily wettable is referred to as a hydrophilic material and one that is wetproof is referred to as a hydrophobic material.

The pressure required to force water into a wetproof, porous material is inversely proportional to the pore size of the material - the smaller the pore size, the higher the intrusion pressure. Once the water is entrapped in a wetproof, porous material, the water will be retained unless some mechanism occurs which removes the water. One mechanism which can cause the entrapped water to be removed from a hydrophobic porous material is for the essentially dry hydrophilic porous material to be placed in direct contact with the hydrophobic material. The relatively dry hydrophilic material then readily absorbs any contacting liquid including that contained in a less absorbent material. The water separator tubes are made of a porous, hydrophilic material and the separator tubes are in contact with the hydrophobic wicking material. The application of a differential pressure across the wall of the separator tubes, which is below the bubble point differential pressure, causes the porous wall to be essentially devoid of water. The separator tubes are thus capable of absorbing water from the wicking as long as the oxygen pressure on the outer diameter (wick side) of the separator tubes is greater than the water pressure within the tubes.

When the water outlet valve of the fuel cell module is open, the water pressure regulator allows water to flow out of the water separator tubes at a rate to maintain the differential pressure across the separator tubes. If the water outlet valve is shut off, the porous wall of the water separator tubes rapidly fills with water and the separator tubes can no longer absorb water from the wicking. If a negligible amount of water is generated at the cathode of the fuel cells (open circuit conditions) and the differential pressure is maintained across the wall of the separator tubes, the separator system is capable of extracting all of the water contained in the wicking. Once the water is extracted from a hydrophobic wick, water must be forced back into the wicking to restore its proper function.

One of the functions of the cell wicking is to supply water to the wick pads near the hydrogen inlets to each cell. The wick pads serve to maintain a high relative humidity on the oxygen side of the SPE, thus permitting water evaporation from the hydrogen side of the SPE for hydrogen inlet humidification. This function is particularly important in supplying water to the upper wick pads where gravity adversely affects the water content of these wick pads.

It is hypothesized that the water separator system on B/U 102 extracted all of the water in the wicking system when an open circuit operation existed for approximately 7 hours after the 1092 operation hour point. There was a tendency for the fuel cell module case to flood after this event, indicating that the product water was cascading over the surface of the wicking. The function of the wicking was at least partially restored by reversing the water flow through the separator system, thus providing a means of forcing water into a portion of the wicking - particularly the wicking adjacent to the separator tubes. The remainder of the wicking was not restored with water, preventing water from being wicked to the upper wick pad. The water removal function was restored after the wicking was partially rewet, inasmuch as the wicking in the vicinity of the separator tubes could readily absorb the product water which reached the vicinity of the separator tubes due to gravity.



A test conducted after a teardown of B/U 102 indicated that a dry wick pad still had sufficient absorption characteristics to remove water from a wet wick. It is therefore hypothesized that the hydrogen humidification function of the lower wick pad was not impaired, particularly after the water content of the cell wicking was partially restored. The hydrogen humidification function of the upper wick pad was impaired since the water content and thus the vertical wicking capability of the upper portion of wicking was never restored after the product water was essentially totally extracted during the event cited above.

New wicking is observed to be readily wettable (hydrophilic) and if the wicking remained wettable throughout the life of the fuel cells, the failure mechanism described above would not occur. Tests of wicking which had been utilized in a fuel cell for more than 1000 hours is observed to be wetproof (hydrophobic) when dry and hydrophilic when wet.

One reference associated with the wetproofing of fabrics makes the general observation that partially wet, wetproof materials readily absorb additional water within the void capacity of the fabric. This explains how a wetproof wick can continue to function as long as the wicking maintains a partial water content.

It is hypothesized that the Dacron wicking in B/U 102 became wetproof during the first 1000 hours of operation. The wetproofing of the Dacron wicking resulted from the cleaning action of the pure water flushing through the wicking with an HF content of 1 to 6.9 ppm. The Dacron wicking continued to function satisfactorily during the first 1000 hours of operation of B/U 102 since the wicking was either being continually supplied with product water or there was no substantial loss of water during dormant periods when the water outlet valve was shut off.

The principal cause of failure of B/U 102 was thus hypothesized to have resulted from the product water valve being left open. The water then was extracted from the wicking, causing a loss of capability of the wicking to supply water to the upper wick pad. The impairment of the mechanism for the humidification of hydrogen near the upper wick pad eventually caused a drying and delamination leading to a failure of the SPE in this region.

4. 2. 5. 3 Laboratory Analysis, B/U 102, Cell 1

After a failure at 1762 hours testing, the B/U 102, Cell No. 1 was released for failure analysis. The analysis showed SPE membrane delamination along the top edge of the inside M and E of Cell No. 1, poor bond strength, greater degradation of the delaminated membrane and O₂ inlet membrane than other sections (as indicated by Cs form IR), no inhibiting membrane contamination, no gross porosity increase in

membrane at O₂ inlets, significantly lower tensile and elongation along bottom edge of "failed" M and E (inside M and E), poor platinization of (1800 hour) used membrane, and an acceptable fluoride ion release under H₂O₂/Fe⁺² test conditions.

Analytical Results

Delamination/Microtome

B/U 102 failed due to cross-membrane leakage located on the inside M and E of Cell No. 1. Initial microscopic examination of Cell No. 1 showed delamination along the top edge of the non-cathode catalyst area of the inside M and E. The delamination appeared to be located "under" the O₂ screen; no other delaminated areas were found. Post-aqua regia microscopic examination confirmed the initial findings with some delamination found in the diamond centers of the same area. Microtomed samples of the delaminated and undelaminated areas were examined microscopically. This examination further substantiated the initial findings of the location of delamination and the presence of leakage in the inside M and E.

Bond Strength - Table XVI

All bond areas tested exhibited poor to non-existent bonds. Blisters between the SPE membrane and polysulfone were apparent along the top and bottom edges of both sides of Cell No. 1, and examination showed strength in these areas only at the flash. The gold-to-polysulfone and gold-to-SPE membrane bonds were non-existent, and the materials could be easily separated. The SPE membrane-to-polysulfone and niobium-to-polysulfone bonds were pulled on an Instron tensile tester (Table XVI), and the data showed bond strength only at flash.

Tensile and Elongation - Table XVII

The tensile and elongation values obtained for B/U 102 used (1800 hour) membranes were generally lower than incoming membrane. Using the same reasoning as outlined in the B/U 101 report, the actual degree of loss compared to a new membrane is in doubt. However, significant decreases in these physical properties were found for those samples taken from the bottom edge of the failed M and E (inside M and E, Cell No. 1). The tensile and elongation values for this area were significantly lower than those found in other areas of Cell No. 1. This indicates a loss of strength in this area.

Water Content - Table XVIII

The water content measurements made on five sections of membrane from the edge toward the center showed the water content of the edge section slightly lower than the adjacent sections. The edge drying was real but probably not of impairing magnitude.

Table XVI

Bond Strength Evaluation - B/U 102, Cell No. 1

<u>Sample Identification</u>	<u>Bond Strength (lb/in.)</u>				
	<u>Au/PS</u>	<u>SPE/PS Peak/Peel</u>	<u>SPE/Au</u>	<u>Nb/PS</u>	
				<u>Out</u>	<u>In Peak/Peal</u>
B-1	0	1.7/0.1	0	0	14.4/1.7
B-2	0	1.3/0.2	0	0	0
B-3	0	2.1/0.1	0	0	0
B-4	0	NG	0	0	0
B-5	0	0	0	0	13.4/0.7
B-6	0	4.8*	0	0	11.8/0.9
B-7	0	8.9*	0	0	11.8/0.9
B-8	0	0	0	0	13.4/0.7

* SPE tore; no peel available.

Table XVII

Tensile and Elongation, SS B/U 102, Cell No. 1

<u>Sample Identification</u>	<u>Tensile, psi</u>	<u>Elongation, %</u>
C-1	2586	162
C-2	1716	81
C-3	1483	57
C-4	2329	139
C-5	2767	155
C-6	2497	151
C-7	2192	122
C-8	2444	143
C-9	2612	155
C-10	1838	95
C-11	1980	121

Table XVIII

Water Content Measurements, SS B/U 102, Cell No. 1

<u>Sample Identification</u>	<u>% H₂O* (as taken from cell)</u>
D-1 Edge 1/4 inch	25.5
D-2 Adjacent 1/4 inch	33.4
D-3 Adjacent 1/4 inch	32.5
D-4 Adjacent 1/4 inch	32.3
D-5 Adjacent 1/2 inch	34.2

$$* \% \text{ H}_2\text{O} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Cesium Form IR Spectra - Table XIX

In an attempt to measure the extent of membrane degradation, cesium form infrared spectra were obtained on sections of Cell No. 1. Higher CO/CF and/or CH/CF values were exhibited in the delaminated area and O₂ inlet areas compared to the other areas of the membrane. This data probably indicates more extensive degradation in these areas.

Contamination - Table XX

Cation contamination analysis of the 1.5 N H₂SO₄ exchange solutions of three membrane areas of Cell No. 1 showed no gross membrane contamination. Glass or similar material was the probable source of the contaminants found, as indicated by the presence of Na, Mg, etc. The level of contamination found was low and would not inhibit membrane function.

Water and Gas Permeabilities - Table XXI

The water and oxygen permeabilities found for the O₂ inlet areas showed no gross porosity increase in the membrane in the wet and dry modes, respectively. Values were of the same order of magnitude as those previously reported for unused membrane.

Membrane Platinization

Two sections of used (1800 hour) membrane from B/U 102, Cell No. 1 were processed by the standard platinization procedure. The resulting platinized membrane was anomalous in as much as the platinum deposited membrane was translucent and brown to black. A microscopic examination of microtomed membrane cross-sections showed the platinum deposited only about 1/8 to 1/4 of the depth of the membrane from either side, leaving a very large portion of the middle of the membrane without platinum.

Peroxide Degradation Testing (H₂O₂/Fe⁺²) - Table XXII

Fluoride ion release under standard H₂O₂/Fe⁺² degradation test conditions was monitored for a membrane section from Cell No. 1. The mg F⁻/g membrane observed was within the allowable limits for incoming membrane.

Table XIX

Cesium Form Infrared Spectra, SS B/U 102, Cell No. 1

<u>Sample Identification</u>	<u>CH/CF</u>	<u>CO/CF</u>
I-1	0.06	0.00
I-2	0.07	0.00
F-1	0.05	0.09
F-2	0.01	0.03
A-4	0.01	0.02
A-6	0.01	0.00
A-7	0.02	0.01

Table XX

Cation IEM Contamination Analysis, SS B/U 102, Cell No. 1

<u>Sample Identification</u>	<u>Cation Contaminants</u>					
	<u>Ca</u>	<u>Co</u>	<u>Fe</u> <u>μg/cm² SPE</u>	<u>K</u>	<u>Mg</u>	<u>Na</u>
H-1	1.5	< 3	< 5	2	1.3	4.0
H-2	1.0	< 3	< 5	1	0.8	1.3
H-3	1.5	< 3	< 5	1.5	0.5	2.3

Table XXI

Permeabilities - Gas and Water at O₂ Inlets (Membrane)

SS B/U 102, Cell No. 1

<u>Sample Identification</u>	<u>Permeability</u>	
	<u>O₂</u>	<u>H₂O</u>
	<u>cm²/atm sec</u>	
I-1	2.3 x 10 ⁻⁸	4.5 x 10 ⁻⁸
I-2	3.4 x 10 ⁻⁸	4.0 x 10 ⁻⁸

Table XXII

Peroxide Degradation

<u>Sample Identification</u>	<u>mg F⁻/g SPE</u>
K1 + K2	0.9

4. 2. 6

CONCLUSIONS AND ACTIONS

The results of the teardown analysis and examination of the failed cells lead to the following conclusions:

- 1) Failure of the buildup was caused by polymer degradation and delamination in Cell 1, which resulted in cross-membrane leakage of O₂ into the H₂ compartment.
- 2) The delaminated areas found at the top edge of membranes examined, were probably caused by inadequate water flow from the H₂ humidification pads into the membrane at the H₂ inlet areas.
- 3) Based on the simulated water system tests, it is indicated that the inadequate water content in the wick pads probably resulted from the shutdowns which occurred at about the 1000 hour point and caused the product water wicking to be pumped dry by the water separator which continued to operate normally. Following the "dry out", the top wick pads would not rewet because of loss of capillarity in the wicking system.
- 4) Another possible cause of inadequate water in the top wick pads is that the design is not capable of supplying sufficient water against gravity to humidify the top inlet H₂ pads.
- 5) Although the membrane bonds did not fail and result in leakage, the bond peel strength data and the observed bond blistering suggest that the bonding system is marginal for 2000 hour life.
- 6) The nylon tie rod insulating washers are not adequate for operation in O₂ at 150°F.

The actions to be taken based on these conclusions are:

- 1) Continue to operate future buildups with prehumidified reactant gases.
- 2) Modify the test facilities to provide automatic shutoff of the product water valve if and when an automatic unit shutdown occurs.
- 3) Introduce modifications to the design of O₂ gasket to provide loading over the entire bond area. This can be accomplished by eliminating the recessed areas in the gasket over the H₂ channels.
- 4) Continue to evaluate possible design modifications which will enable the unit to operate using dry reactants. This will be done using laboratory 3 x 3 inch fixtures.



- 5) Replace the nylon tie rod washers with a more suitable material.
- 6) The remaining two cells will be stored for future hardware displays or other laboratory analyses since they are no longer operable by virtue of the plugged hydrogen inlet tubes and deformed sealing surfaces at the external manifolds as a result of the stack failure.

5.0

Recommendations

- a. Utilizing the three (3) cell assemblies that completed 2011 hours of life in a three-cell build-up (B/U #101A), life testing should be continued under operating conditions similar to B/U #101 until failure occurs. The modified oxygen gasket to provide improved back-up support for the bonded area of the cell assembly should be included in B/U 101A for evaluation. The stop/start procedures for the extended testing should be modified to more nearly simulate the proposed procedures for space vehicle operation.
- b. A small stack test unit (4 cell assemblies) of the same configuration as B/U #101 should be fabricated and life tested at cell temperature of 180°F with prehumidified reactants in order to evaluate the capability for improved performance.
- c. A small stack test unit (4 cell assemblies) of a modified cell configuration, as indicated by the matrix evaluation for further reducing the HF level in the product water, should be fabricated and life tested. Various operating conditions should be correlated to HF level in the product water, i. e. :
- ° Prehumidified reactants at 150°F
 - ° Prehumidified oxygen only at 150°F
 - ° Prehumidified reactants at 180°F
 - ° Prehumidified oxygen only at 180°F.
- d. A full stack of 40 cell assemblies should be fabricated to the B/U 101 configuration and life tested at 150°F with prehumidified reactants.
- e. A full stack of 40 cell assemblies should be fabricated to the same configuration as the 4 cell assembly stack above which is designed to reduce the HF levels below those experienced with the B/U 101 configuration. This full stack should be life tested with prehumidification and at temperatures proven in the above 4 cell assembly stack.
- f. A flight weight prehumidifier for both hydrogen and oxygen should be designed, fabricated and life tested for integration into a fuel cell module.
- g. The ancillary components for a fuel cell module that were life tested under Contract NAS 9-11033 for 2000-2500 hours at 150°F should be continued on life test at 180°F.
- h. A complete Engineering Model of the 5 KW fuel cell module (2 stacks of 40 cell assemblies each) should be fabricated and life tested.

i. A continuing program of matrix evaluations should be conducted in the laboratory to complete the understanding of failure mechanisms.

j. An investigation and evaluation program should be pursued to determine alternate bonding materials and procedures in order to eliminate performance losses associated with present materials.